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ELECTRO-CHEMICAL ANALYSIS.

SMITH.

RICHTER'S CHEMISTRIES.

AUTHORIZED TRANSLATIONS.

BY EDGAR F. SMITH, F.C.S., M.A., PH.D.,

Professor of Chemistry, University of Pennsylvania; Member of Chemical Societies of Berlin and Paris, etc.

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ELECTRO-CHEMICAL ANALYSIS.

BY

EDGAR F. SMITH,

PROFESSOR OF ANALYTICAL CHEMISTRY, UNIVERSITY OF PENNSYLVANIA.

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PREFACE.

In preparing this little volume the author has had constantly in view the needs of a large class of students of analytical chemistry desirous of becoming acquainted with the methods of quantitative analysis by electrolysis; these are daily acquiring greater importance, and being introduced and applied wherever possible.

The larger texts devoted to analysis have omitted electrolysis from their pages, thus rendering its special treatment necessary and desirable.

The plan adopted in the following pages in presenting this subject has been to give a brief introduction upon the behavior of the current toward the different acids and salts, a short description of the various sources of the electric energy; its control and measurement; after which follow a condensed history of the introduction of the current into chemical analysis, and sections relating to the determination and separation of metals, as well as the oxidations possible by means of the electric agent.

In using this book as a guide, the student is earnestly recommended to perform the determinations of each metal as indicated in the text. The details have been made sufficiently full, and clear enough, it is hoped, for the most inexperienced analyst. Additional skill and valuable experience are acquired with each trial, so that, when the section treating of separations is reached, the work there outlined will be performed without difficulty. Before commencing the determination of any one metal read, if possible, its literature.

The methods of determination and separation given preference are not those of any one individual, but have been selected from all sources after an experience of many years, care being taken to present only those which actual tests have shown to be reliable and trustworthy.

It has not been considered advisable to include an outlined electrolytic analysis of alloys and minerals in the text, inasmuch as the experience gained in performing the analyses already described there will have given the analyst such a fund of experience that the course to be pursued in special cases will readily suggest itself.

The author would here acknowledge his indebtedness to the various writers on electrolysis, whose publications he has freely used, to the editors of the different journals consulted, to friends who have made kindly suggestions, and to his brother, Dr. Allen J. Smith, who prepared all the drawings from which the illustrations of the text were made. S.

University of Penna.,
Philadelphia, Sept., 1890.

TABLE OF CONTENTS.

PAGE
INTRODUCTION, ... 9–10
ACTION OF THE ELECTRIC CURRENT UPON ACIDS AND SALTS, 10–13
OHM, VOLT, AMPERE, ... 13–14

SOURCES OF ELECTRIC CURRENT—

Grenet Battery, Leclanché Cell, Daniell Cell, Meidinger Cell, Crowfoot Cell, Bunsen and Grove Batteries, Magneto-Electric Machines, Storage Cells, Thermopile, ... 14–25

REDUCTION OF THE CURRENT—

Rheostat, Resistance Frame, ... 25–29

MEASURING CURRENTS—

Voltameter, Amperemeter, ... 29–32
HISTORICAL SKETCH, ... 32–46

SPECIAL PART.

1. DETERMINATIONS OF METALS, ... 47–89
2. SEPARATION OF METALS, ... 89–108
3. OXIDATIONS BY MEANS OF THE ELECTRIC CURRENT, . 108–113
INDEX, ... 115

ABBREVIATIONS.

JAHRB. . . . . = *Jahresbericht der Chemie.*
C. R. . . . . = *Comptes Rendus.*
JR. F. PKT. CH. . . . = *Journal für praktische Chemie.*
ANN. . . . . = *Annalen der Chemie und Pharmacie.*
Z. F. A. CH. . . . . = *Zeitschrift für analytische Chemie.*
BER. . . . . . . = *Berichte der deutschen chemischen Gesellschaft.*
AM. JR. SC. AND AR. = *American Journal of Science and Arts.*
AM. PHIL. SOC. PR. . = *Proceedings of the American Philosophical Society.*
AM. CH. JR. . . . . = *American Chemical Journal.*
AM. CH. . . . . . . = *The American Chemist.*
JR. AN. CH. . . . . = *Journal of Analytical Chemistry.*
JR. FR. INS. . . . . = *Journal of the Franklin Institute*, Phila.
BERG-HÜTT. Z. . . . = *Berg-und Hüttenmännische Zeitung.*
B. S. CH. PARIS . . = *Bulletin de la Société Chimique de Paris.*
CH. NEWS. . . . . . = *Chemical News.*
DING. P. JR. . . . . = *Dingler's Polytechnisches Journal.*
G. CH. ITAL. . . . . = *Gazetta chimica italiana.*

ELECTRO-CHEMICAL ANALYSIS.

INTRODUCTION.

Many chemical compounds are decomposed when exposed to the action of an electric current. A decomposition of this kind is called *electrolysis*, while the substance undergoing change is termed an *electrolyte*. The products of the decomposition are the *anions* and *cathions*, or those (1) which separate at the *anode*, the positive electrode or pole (+ P) of the battery, and (2) those separating at the *cathode*, the negative electrode or pole (— P) of the battery.

This behavior of compounds has become of great service to the analyst, inasmuch as it has enabled him to effect the isolation of metals from their solutions, and by carefully studying the electrolytic behavior of salts it has been possible for him to bring about quantitative determinations and separations.

The electrolytic method of analysis is especially inviting, since it permits of clean, accurate and rapid determinations where the ordinary methods yield unsatisfactory results. This statement is readily confirmed on recalling the gravimetric methods usually employed in the estimation of copper, mercury, cadmium, bismuth, tin, etc., etc. That this assertion may be the conviction of every student of analysis, the writer would call attention first to the course of the current in solutions of some of the more frequently occurring salts; after which will follow a brief account of the various modes of obtaining the electric current, how it may be measured and how controlled. Finally, all the metals, which have been studied electrolytically, will be taken up in detail, and their various determinations will be followed by a sufficient number of separations to show, at least in part, how widely the electrolytic method of analysis may be applied.

1. ACTION OF THE ELECTRIC CURRENT UPON ACIDS AND SALTS.

		At the — Pole.	At the + Pole.
Hydrochloric acid	+ the current	= Hydrogen	+ Chlorine.
Copper chloride	+ " "	= Cu	+ Cl_2.
Zinc chloride	+ " "	= Zn	+ Cl_2.
Nitric acid	+ " "	= H	+ NO_2 + O.

In this last case the hydrogen further acts upon more nitric acid and produces ammonia (NH_3) and water.

Lead nitrate + the current = Pb + NO_2 + O.

The oxygen liberated here attacks a second molecule of lead nitrate, and produces lead peroxide, $Pb(NO_3)_2 + O_2 = PbO_2$, which deposits upon the positive electrode.

$$\begin{array}{lll} & \text{At the} & \text{At the} \\ & -\text{ Pole.} & +\text{ Pole.} \\ \text{Copper nitrate} + \text{the current} = & Cu & + (NO_3)_2. \\ \text{Sulphuric acid} + \text{“} \quad \text{“} \quad = & H_2 & + SO_4. \end{array}$$

Secondary changes frequently occur in these decompositions; thus, in the last example the SO_4 reacts with the water present: $SO_4 + H_2O = H_2SO_4 + O$, the oxygen going to the positive electrode. In the electrolysis of copper sulphate, which is analogous to sulphuric acid, secondary changes also occur.

$$\begin{array}{lll} & \text{At the} & \text{At the} \\ & -\text{Pole.} & +\text{ Pole.} \\ \text{Potassium sulphate} + \text{the current} = & K_2 & + SO_4 \end{array}$$

In this decomposition the liberated potassium acts upon water, with the liberation of hydrogen and the formation of potassium hydroxide.

Bourgoin observed the following changes with formic, acetic and oxalic acids, and their salts:—

1. *Formic Acid.*—The decomposition may be expressed in two equations—

$$\begin{array}{lcll} (a)\ CH_2O_2 & = & H & + (CHO + O). \\ & & -\text{ Pole} & \quad +\text{ Pole} \\ (b)\ 2(CHO + O) & = & CH_2O_2 + & \quad CO_2. \end{array}$$

The decomposition of sodium formate yields carbon dioxide and formic acid at the anode, and hydrogen and sodium hydroxide at the cathode.

2. *Acetic Acid.*—The electrolysis of the dilute acid affords hydrogen at the negative electrode, and at the positive electrode a mixture of oxygen, carbon dioxide and a small quantity of carbon monoxide.

3 *Oxalic Acid.*—The electrolysis of this acid with a current obtained from four Bunsen cells gave decompositions which may be expressed as follows :—

$$C_2H_2O_4.2H_2O + \text{current} = \underset{-\text{ Pole.}}{3H_2} + \underset{+\text{ Pole.}}{2CO_2 + O_2};$$

the oxygen reacts upon additional acid :

$$2C_2H_2O_4 + 2H_2O + O_2 = 4CO_2 + 4H_2O,$$

so that the final products are pure carbon dioxide at the positive electrode and hydrogen at the opposite pole. The decomposition of potassium oxalate may be formulated in the following way :

$$C_2K_2O_4 = \underset{-\text{ Pole.}}{K_2} + \underset{+\text{ Pole.}}{2CO_2};$$

the liberated metal and the carbon dioxide then react further :—

$$2H_2O + K_2 = 2KOH + H_2 \text{ and } 2CO_2 + 2KOH = 2KHCO_3.$$

When exposed to the same influence ammonium oxalate yields hydrogen at the negative electrode, and hydrogen ammonium carbonate at the positive electrode. The latter compound further breaks down into ammonia and carbon dioxide.

Succinic acid is electrolysed with difficulty. In its decomposition the products which have generally been observed at the positive electrode were oxygen and the two oxides of carbon. By electrolysing sodium succinate Kekulè obtained hydrogen at the cathode, and carbon dioxide and ethylene at the anode.

Tartaric acid + the current gave at

— Pole.	+ Pole.
hydrogen	acetic acid, carbon dioxide, carbon monoxide and oxygen ;

while with potassium tartrate the products were hydrogen and potassium at the cathode and acid potassium tartrate, carbon dioxide, carbon monoxide and oxygen at the anode. An alkaline solution of potassium tartrate gave hydrogen at the cathode and at the anode, acetic acid, the oxides of carbon, oxygen and ethane (C_2H_6).

The above examples will suffice to indicate the nature of the decomposition due to the current; they will assist very materially in understanding the changes occurring in ordinary electrolytic analyses. For further particulars in this direction, consult Tommasi's *Traité Théorique et pratique d'Électrochimie*.

2. OHM, VOLT AND AMPERE.

These terms may be defined as follows:—

The *ohm* is the unit of resistance. Its value is represented by a column of mercury 1 sq. mm. in cross-section, and 106.2 cm. in length at the temperature 0° C.

The *volt* is the unit of electromotive force (E. M. F.). It is the E. M. F. which gives a current of one ampere through a resistance of one ohm.

The *ampere* is the unit of current. It is the current which, under an electromotive force of one volt, flows through a circuit offering a resistance of one ohm.

$$A = \frac{V}{O}.$$

3. SOURCES OF THE ELECTRIC CURRENT.

The electric energy required for quantitative analysis has been variously furnished by batteries of well-known types, magneto-electric machines, dynamos, thermo-piles, and electrical accumulators or storage cells. A brief description of some of these may be properly introduced here.

The *Grenet* cell or *Bichromate Battery* (Fig. 1) consists of two plates of carbon (K) and one of zinc (Z), movable by means of the handle, *a*. This is a convenient arrangement, as it allows of easy interruption of the current. The liquid to be used in this cell consists of potassium bichromate (1 lb.), strong sulphuric acid (2 lbs.), and water (12 lbs.). In mixing these, the probable chemical change is:—

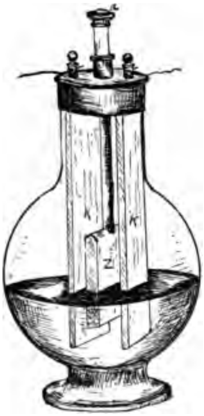
$$K_2Cr_2O_7 + 7H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O + 6H_2SO_4.$$

The chemical action in the cell, when the current passes, may be expressed by the equation:—

$$2CrO_3 + 6H_2SO_4 + 3Zn = Cr_2(SO_4)_3 + 3ZnSO_4 + 6H_2O.$$

The writer found four cells of this type (capacity two quarts) very serviceable in the electrolysis of solutions of cadmium, uranium, molybdenum and other metals. No disagreeable fumes arise from cells of this class. The electromotive force is about two volts, and the internal resistance low. The Grenet cell loses in intensity when used for long periods, but regains its value when it has remained out of action for some time.

FIG. 1.



Leclanché cell (Figs. 2 and 3).—Two forms of this cell are in use. In the first, to the left of the figure, there is a zinc rod, immersed in a solution of ammonium chloride, and a carbon plate inside a porous cup, tightly packed with a mixture of manganese dioxide and broken gas carbon. The porous cup is only intended to hold the mixture in position. There is but one liquid, and that a strong solution of ammonium chloride. The *E. M. F.* of this cell equals 1.47 volts; it decreases rapidly when sending strong currents. It is inferior to the Daniell cell when a steady current is desired for a long period.

FIG. 2.

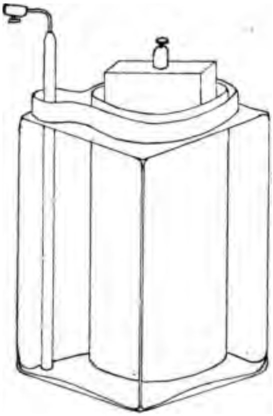
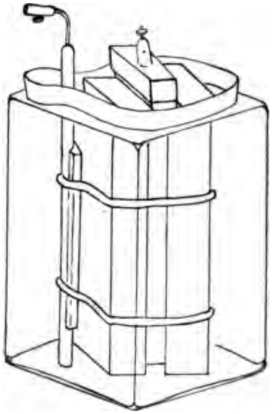


FIG. 3.



The chemical action in cells of this kind Ayrton expresses as follows:—

(Before sending the current)—

$$k\,C + l\,(MnO_2) + m\,(NH_4Cl) + n\,Zn.$$

(After sending the current)—

$$k\,C + (l - 2)(MnO_2) + (m - 2)(NH_4Cl) + (Mn_2O_3) + 2(NH_3) + (H_2O) + (ZnCl_2) + (n - 1)(Zn).$$

The letters *k*, *l*, *m*, *n* represent indefinite amounts of the acting substances.

In the modified Leclanché cell the porous cup is not needed, as compressed prisms of manganese dioxide, gas carbon and shellac are used around the carbon plate.

The *Daniell* cell (Fig. 4) consists of a glass jar, the porous cup T, and a cylinder of zinc (Z), the negative pole. Outside of the porous cup is the sheet-copper cylinder K. The zinc is the negative electrode, and the copper the positive electrode. The zinc stands in dilute sulphuric acid (1 : 20), and the copper in copper sulphate. Zinc sulphate often replaces the sulphuric acid. The chemical action in the cell is probably:—

$k\,(Cu) + l\,(CuSO_4)$.	(Before sending the current.)	Porous partition.	$m\,(ZnSO_4) + n\,(Zn)$.
$(k + 1)(Cu) + (l - 1)(CuSO_4)$.	(After sending the current.)		$(m + 1)(ZnSO_4 + (n - 1)(Zn)$. (Ayrton).

The *E. M. F.* of this cell is about 1.07. The *Meidinger* (Fig. 5) and *Crowfoot* (Fig. 6) cells are modifications of the Daniell, and very serviceable in electrolytic

Fig. 4.

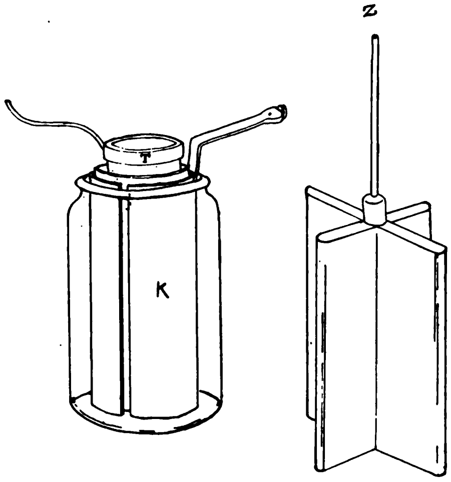


Fig. 5.

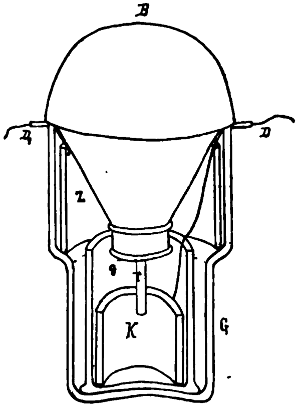
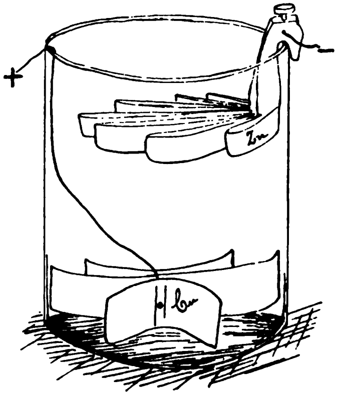


Fig. 6.



work when currents of low intensity are desired. In the sketch of the Meidinger cell, *G* is a large glass jar; *g*, a small glass vessel, in which stands the copper cylinder, K (+ P). Z (— P) is a cylinder of zinc. B contains the supply of copper sulphate crystals.

The current from either of these batteries remains quite constant for long periods. The cells themselves do not require much attention. Half a dozen of either of these forms will do nearly all the electrolytic work of an ordinary laboratory. The "Crowfoot" form can be readily and cheaply prepared. Rejected acid bottles, after removing the neck and upper portions, answer well as jars.

If currents of greater *E. M. F.* are required, the Bunsen (Fig. 7) or Grove cell (Fig. 8) should be used. In the former there is zinc in dilute sulphuric acid, or a mixture of potassium bichromate and sulphuric acid, and a carbon plate in a cup of nitric acid. It is a less expensive cell than the Grove, as platinum is not employed. It is not so readily handled, and consumes more nitric acid. Its electromotive force is somewhat less than that of the Grove form. In the latter there is a strip of platinum (P) in concentrated nitric acid (in the porous cup, *x*), and zinc (ZZ) in dilute sulphuric acid (one pint acid and ten pints water). The *E. M. F.* is 1.93 volts. When acting, N_2O_4 is set free; this can be in a measure suppressed by adding ammonium chloride to the nitric acid. The chemical changes occurring in the Bunsen and

Grove cells are very similar. Ayrton expresses them as follows:—

(Before current is sent)—

$$k\,(\mathrm{Pt}) + l\,(\mathrm{HNO_3}). \qquad \text{Porous partition.} \qquad m\,(\mathrm{H_2SO_4}) + n\,(\mathrm{Zn}).$$

(After sending current)—

$$k\,(\mathrm{Pt}) + (l - 2)(\mathrm{HNO_3}) + (\mathrm{N_2O_4}) + (2\mathrm{H_2O}). \qquad \text{Porous partition.} \qquad (m - 1)(\mathrm{H_2SO_4}) + (\mathrm{ZnSO_4}) + (n - 1)(\mathrm{Zn}).$$

FIG. 7.

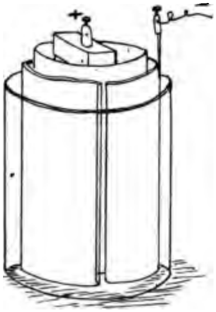
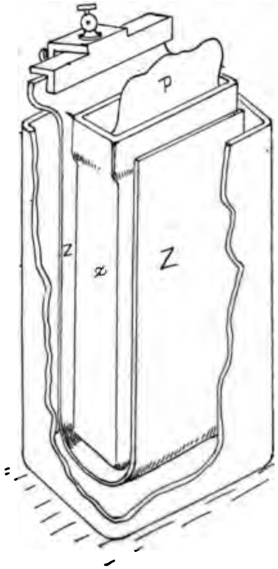


FIG. 8.



The internal resistance of the Grove cell is small. To obtain good results both the Bunsen and Grove cells require constant attention.

In amalgamating the zincs in any of the preceding batteries, first allow them to remain over night in very dilute hydrochloric acid, then immerse in mercury, and with a wet cloth rub the latter into the metal. This should be done once a week, when the cells are in daily use. For further information upon batteries, consult Ayrton's *Practical Electricity*.

Magneto-electric machines, and dynamos have been used to some extent in electrolytic decompositions, but a detailed description of their construction will not be given. This may be found in Classen's *Analysis by Electrolysis*, pp. 21–35 (Herrick's translation).

Thermo-piles have also been used to furnish currents for electrolytic work. Their use has been objected to upon the ground that the currents afforded by them are rarely strong enough for the greater number of determinations and separations, and again they are easily broken and difficult to repair. The forms generally met with are those recommended by Clamond and Noë.

The Clamond thermo-pile is pictured in Fig. 9. 1 is a perspective view of the same; 2 represents a vertical section, and 3 a basal section, showing the bars and armatures. The elements consist of bars of a zinc and antimony alloy, and a strip of sheet-iron. These are arranged in circles, as indicated in 3; they are placed one above the other. In 3, *B* represents the bars of zinc and antimony alloy, while the tinned

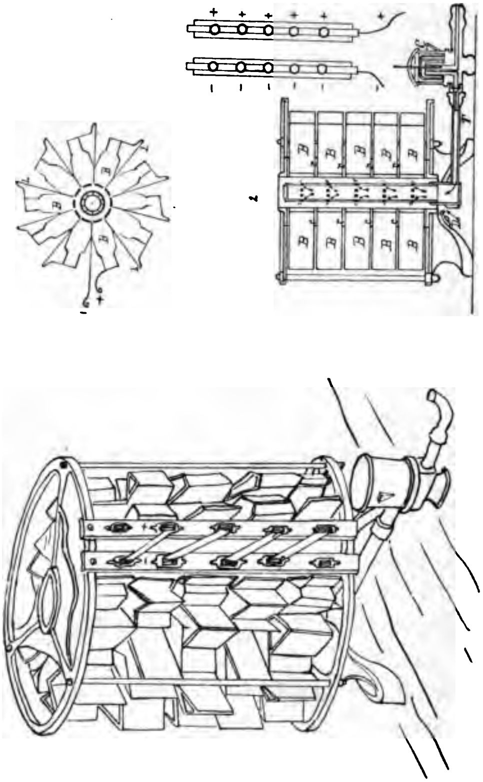


FIG. 9.

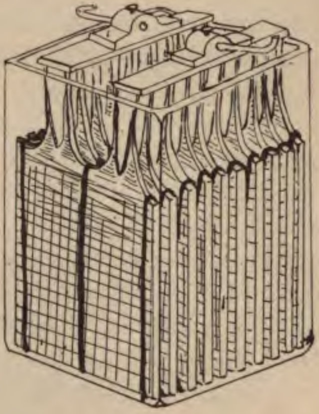
sheet-iron plates are marked *L*. The sheet-iron serves to conduct the current from one element to the other; hence, these strips rest upon the bars *B*. Heat expands the latter, and in consequence renders the contact more intimate. The single elements, as well as the circles of elements, are separated from each other by plates of asbestos (see *r* in 2). The cylinder itself consists of a series of such circles. The welded points of the bars are all directed to the centre of the cylinder. The gas flames are prevented from coming in immediate contact with them by the asbestos lining of the cylinder. As gas is employed to furnish the necessary heat, in the middle of the cylinder will be observed a clay tube (*A*) provided with apertures (2 and 3). The gas enters through the Giroud regulator *C* (1 and 2), which makes it possible to maintain a uniform temperature, and a constant current. From *C* it is conducted to *A*, through *T*, into which air is admitted by suitable apertures. The mixture of air and gas burns at the openings in *A*. Additional air is supplied through *D*. Light the gas jets from above, after removing the cover. The poles of each ring of elements end in binding screws, thus enabling the operator to connect any number of them, depending upon the external resistance (Z. f. a. Ch., 15, 334).

When in excellent condition, thermo-piles are said to yield a current equivalent to 400–500 c.c. oxyhydrogen gas per hour. Those persons who may desire fuller information upon this type of battery are referred to the following

LITERATURE:—Z. f. a. Ch., **14**, 350; **17**, 205; Ding. p. Jr., **224**, 267; Z. f. a. Ch., **18**, 457; **25**, 539.

The best source of electric energy, for electrolytic purposes, is unquestionably the storage cell (Fig. 10).

FIG. 10.



The illustration represents a cell of the Julien type. It contains nineteen alternating plates of lead and lead dioxide. Each of these is five and three-fourths inches square. The exciting liquid is sulphuric acid of sp. gr. 1.2. The *E. M. F.* of such a cell is a little more than two volts. The current is very constant.

Cells of this kind can be charged from primary batteries, or better, by means of a dynamo. In any community where electric lighting is employed it is possible to have the charging done at little expense, and in factories where there is always sufficient power, a small dynamo could easily be arranged for this purpose, so that almost any number of cells could be kept in condition for work. The iron estimations required by any establishment could be rapidly and accurately made with three cells of this type; little attention would be demanded from the chemist. While storage cells can be used in almost every description of electrolysis, there are a great many cases where economy would suggest the use of the cheaper batteries, *e.g.*, the Crowfoot. Consult the following literature upon storage batteries:—

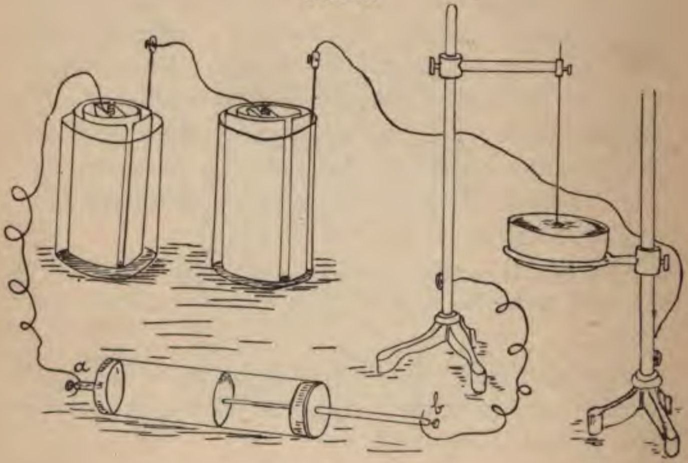
Proceedings of the Royal Society, June 20th, 1889; Transactions of Am. Inst. Mining Engineers (Electrical Accumulators, Salom), Feb., 1890.

Having thus briefly described the more important current-producers, the means of regulating the current may be next considered.

4. REDUCTION OF THE CURRENT.

When a battery gives a current that generates 10 c.c. oxy-hydrogen gas per minute, and work is to be done which can easily be performed by an expenditure of energy not exceeding 3 c.c. oxy-hydrogen gas per minute, it will become necessary to reduce the strong current. Persons acquainted with practical physics will promptly suggest the resistance coils found in physical laboratories, as suitable for this purpose. They are, on the whole, quite satisfactory, and have been thus utilized, although simpler and more convenient current-reducers have made their appearance in recent years. A few of these later appliances may be mentioned:—

FIG. 11.



1. The current may be sent through a solution (saturated) of zinc sulphate, contained in a large glass cylinder, about 22 cm. long and 8.5 cm. in diameter. In one experiment the current is passed from *a* to *b* (Fig. 11), and in the next from *b* to *a*. "The rod *b*,

with one zinc pole, is pushed toward the zinc pole *a*, until the current reaches the desired strength." It is well to amalgamate the zincs from time to time. We are indebted for this piece of apparatus to Classen, who has also described another simple rheostat (Fig. 12) (Ber., **21**, 359). In this apparatus the current enters at *a*, travels the German silver resistance *n*, and returns through *b* to the battery. In the performance of electrolytic depositions the platinum vessels, serving as negative electrodes, may be connected with any one of the binding-posts from 1–20. This makes it possible for the analyst to execute eight different determinations at the same time. To show the influence of this apparatus, a current from five Bunsen cells, generating 68 c.c. oxy-hydrogen gas per minute, was allowed to act upon copper solutions contained in six vessels. The current at binding-post 1 was found to be equal to 3.75 amperes; at 2, it equaled 2.617

FIG. 12.

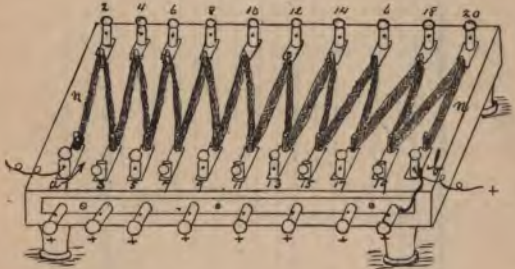
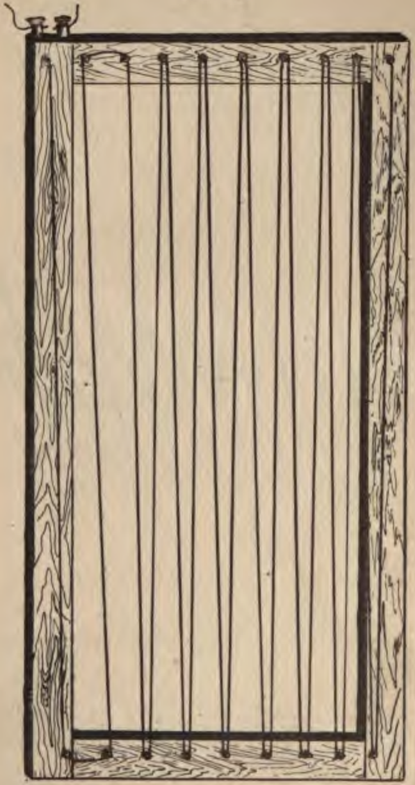


Fig 13.



amperes; at 3, 2.085 amperes; at 4, 1.911 amperes, etc., until at 20 it was only 0.098 of an ampere.

To better understand these figures it should be remembered that an ampere equals 10.436 c.c. oxyhydrogen gas per minute, or it is equivalent to a current which will precipitate 19.69 mg. of metallic copper, or 67.1 mg. of metallic silver in one minute.

For a larger form of apparatus somewhat similar to that described above see Ber., **17**, 1787.

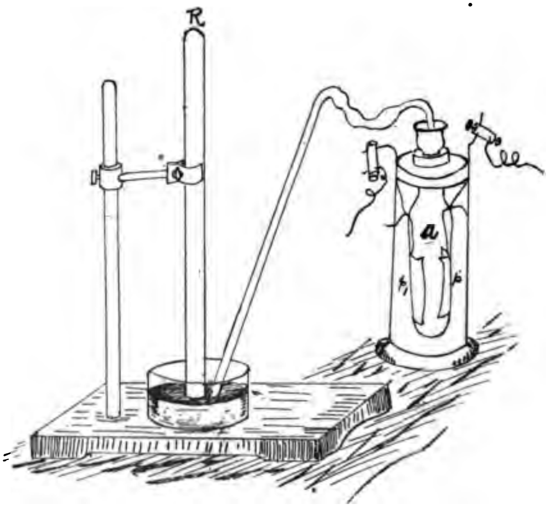
The writer has for some time employed a much simpler current-reducer, which has the advantage of cheapness and ready construction to recommend it. It consists of a light wooden parallelogram, about six feet in length. Extending from end to end, on both sides, is a light iron wire, measuring in all about 500 feet (Fig. 13). With the binding-posts at *a* and *b*, and a simple clamp, it is possible to throw in almost any resistance that may be required. It answers all practical purposes.

LITERATURE.—v. Klobukow, Jr. f. pkt. Ch., **37**, 375; **40**, 121.

5. MEASURING CURRENTS, VOLTAMETER, AMPEREMETER.

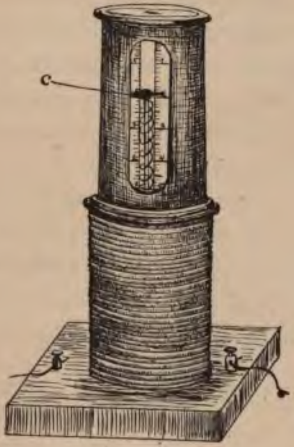
In every analysis by electrolysis it is advisable that the strength of the acting current should be known. The simplest and most convenient apparatus for this purpose is the Bunsen voltameter (Fig. 14). The inner tube *a*, containing sulphuric acid of sp. gr. 1.22, stands in a large cylinder of water to cool it. The liberated hydrogen and oxygen are collected over water in the eudiometer tube R; p and p′ are platinum electrodes. In all accurate experiments the volume of gas should always be reduced to 0° and 760 mm.

FIG. 14.



pressure. Some chemists substitute a galvanometer (tangent or sine) for the voltameter. The deflection of the needle by the current measures the strength of the latter. "In order to express in terms of chemical action the deflection of the needle, it is placed in the same current with a voltameter, and the deviation of the needle is observed, as well as the volume of electrolytic gas (reduced to 0° and 760 mm. pressure), which is produced in a minute. Placing the volume equal to v, the quotient $\frac{v}{\tan.\ a}$ gives the standard value for the galvanometer. If this standard value is denoted by R, the strength I, of a current, which produces the deviation a, is $I = R \tan.\ a$."

FIG. 15.



The writer has found the amperemeter of Kohlrausch (Fig. 15) very satisfactory, especially in cases where strong currents are employed. In this instrument the current travels through an insulated wire surrounding a bar of soft iron. The latter, in its magnetized state, attracts the needle *C*, attached to a spiral. *C* moves over a graduated face (in amperes), and its deflection gives at once the strength of the current in amperes.

In electrolytic work of any kind it is advisable that the apparatus intended to measure the current strength should be in the circuit during the entire decomposition, for it is only in this way that we can expect to effect separations without encountering unpleasant difficulties. It is necessary to know just what energy is required, and then to so regulate the current that the same is approximately maintained throughout the entire determination.

Before taking up the description of the details to be observed in the electrolytic precipitation of individual metals, it may not be uninteresting to briefly trace the history of the introduction of the electric current into chemical analysis.

6. HISTORICAL.

Although the early years of this century show considerable activity in electrical studies, the efforts were mainly directed to the solution of the physical side of electrolysis. To Gaultier de Claubry probably belongs the credit of having first (1850) applied the current to the detection of metals when in solution. His efforts were wholly directed to the isolation of metals

Roy Ravone Rogers

from poisons by depositing the same upon plates of platinum. When the precipitation was considered finished the plates were removed, carefully washed, and the deposited metals brought into solution with nitric acid, and there tested for and identified by the usual course of analysis. The current was evidently very feeble, as the time recorded as necessary for the deposition varied from ten to twelve hours. Gaultier considered this method reliable in all instances, but especially recommends it for the separation of copper from bread. In testing for zinc he employed a strip of tin as anode, but states that a platinum plate will answer as well.

In Graham-Otto's Lehrbuch der Chemie (1857) it is stated that the oxygen developed at the positive electrode readily induces the formation of peroxides; . . . that lead and manganese peroxides are deposited, from solutions of these metals, upon the positive electrode of the battery; . . . that the point of a platinum wire, when attached to the anode of a cell, is therefore a delicate means of testing for manganese and lead. In the same text the oxidizing power of the anode is nicely shown by the following simple experiment: A piece of iron, in connection with the positive electrode of the battery, is introduced into a V-shaped glass tube containing a concentrated solution of potassium hydroxide, while a platinum wire running from the negative electrode projects into the other limb of the vessel. In a short time ferric acid appears around the anode, and is recognized by its color.

C. Despretz (1857) described the decomposition of certain salts by means of the electric current, and remarked that, while operating with solutions of the acetates of copper and lead, he expected both metals would be deposited upon the negative pole, and was much surprised to find that the lead separated as oxide upon the anode at the same time that the copper was deposited upon the cathode. The results were the same when experiments were conducted with the nitrates and pure acetates. With manganese no deposition took place upon the negative electrode, but a black oxide appeared at the opposite pole. Potassium antimonyl tartrate gave a crystalline metallic deposit of antimony at the cathode, and upon the anode a yellowish-red coating, supposed to be anhydrous antimonic acid. Bismuth nitrate yielded a reddish-brown deposit at the positive electrode. Despretz concludes his paper by stating that although the facts were few in number, yet they were new in so far as they concerned lead, antimony and manganese; and, furthermore, that the separation of copper from lead by the current was almost perfectly complete.

Three years later (1860) Charles L. Bloxam recommended the process of Gaultier for the detection of metals in organic mixtures, although it may not be improper to add that Smee (1851), in his work on electrometallurgy, asserts that Morton was the first person to employ the electric current for the isolation of metals from poisonous mixtures. However this may be, the fact remains that Bloxam did use the current quite extensively for this purpose, and while he claims no quantitative results for the method, the apparatus employed by him and his subsequent work in this direction deserve great credit.

To detect arsenic electrolytically Bloxam made use of a glass jar, four cubic inches in capacity, closed below by parchment, which was tightly secured by means of a thin platinum wire. In the neck of the jar was a large cork, through which passed a glass tube bent at a right angle. This tube was intended to serve as a means of escape for the gases liberated within the jar. The platinum wire from the negative electrode was also held in position by the cork. The portion of the wire within the jar was attached to a platinum-plate dipping into the arsenical mixture containing dilute sulphuric acid. The jar with its contents stood in a wide beaker, filled with water, into which dipped the positive electrode of the battery. Under the influence of the current, metals like antimony, copper, mercury and bismuth separated upon the platinum plate of the negative electrode, while arsine was liberated and escaped through the exit-tube into some suitable absorbing liquid. To ascertain what metal or metals had separated upon the cathode, the plate attached thereto was removed, after the interruption of the current, and treated with hot ammonium sulphide. Upon evaporating this solution an orange-colored spot remained if antimony had been previously present. If a metallic deposit continued to adhere to the foil the latter was acted upon by nitric acid to effect the solution of the remaining metals.

J. Nicklès (1862) precipitated silver with the current obtained from a zinc-copper couple. The positive electrode consisted of a piece of graphite, taken from a lead-pencil, while a thin, bright copper wire constituted the negative electrode. The silver separated upon this. The current was very feeble, for hydrogen was not liberated at the cathode. Nicklès also suggested the reduction of large quantities of silver from the solution of its cyanide by this means. To obtain the silver he advised using a cylindrical cathode constructed from some readily fusible alloy, so that after the reduction was finished, the other metals might be easily melted out and leave a silver plate. Copper, lead, bismuth and antimony were separated electrolytically, by Nicklès, from textiles.

In 1862 A. C. and E. Becquerel resumed their electro-chemical investigations, first begun some thirty years previously. Their experiments seem to have been aimed chiefly toward the reduction of metallic solutions upon a large scale, caring not for the quantitative estimation of metals, but seeking rather a rapid and satisfactory technical isolation process.

Wöhler (1868) found that when palladium was made the positive conductor of two Bunsen cells, and placed in water acidulated with sulphuric acid, it immediately became covered with alternating, bright, steel-like colors. He regarded the coating as palladium dioxide since it liberated chlorine when treated with hydrochloric acid, and carbon dioxide when warmed with oxalic acid. Black amorphous metal separated at the cathode. Its quantity was slight. Under similar conditions lead also yields the brown dioxide, and the same may be said of thallium. Osmium, in its ordinary porous form, at once becomes osmic acid When caustic alkali is substituted for the acid the liquid rapidly assumes a deep yellow color, while a thin deposit of metal appears upon the cathode. Ruthenium behaves similarly when applied in the form of powder. Osmium-iridium, a compound decomposed with difficulty under ordinary circumstances, immediately passes into solution when brought in contact with the positive electrode of a battery placed in a solution of sodium hydroxide, and imparts a yellow color to the alkaline liquid. A black deposit of metal slowly makes its appearance upon the negative pole.

The experiments, thus far described, are qualitative in their results. The first notice of the quantitative estimation of metals electrolytically was that of Gibbs (1864), when he published the results he had obtained with copper and nickel. Luckow, in alluding to this work a year later (1865), says: "I take the liberty to observe that so far as the determination of copper is concerned, I estimated that metal in this manner more than twenty years ago, and as early as 1860 employed the electric current for the deposition of copper quantitatively in various analyses." It was Luckow who proposed the name *Elektro-Metall Analyse* for this new method of quantitative analysis. According to this writer the current may be applied as follows:—

1. To dissolve metals and alloys in acids by which they would not be affected unaided by the electric current.

2. To detect metals like manganese and lead (silver, nickel, cobalt); separating them in the form of peroxides; also manganese as permanganic acid.

3. To separate various metals, *e.g.*, copper and manganese from zinc, iron, cobalt and nickel.

4. To deposit and estimate metals quantitatively, in acid, alkaline and neutral solutions.

5. For various reductions, *e.g.*, silver chloride, basic bismuth chloride and lead sulphate, in order that the metals in them may be determined. To reduce chromic acid to oxide, *e.g.*, potassium bichromate acidulated with dilute sulphuric acid.

These applications embrace nearly all that has since been accomplished by the aid of the current. In the same article to which Luckow calls attention to the facts recorded above, he describes minutely the method pursued by him in the precipitation of metals. Reference to these early experiments will show with what care and accuracy every detail was worked out. Luckow also announced "that all the lead contained in solution was deposited as peroxide upon the positive electrode, and might be determined from the increased weight of the latter." This observation was fully confirmed by Hampe and, later, by W. C. May.

Wrightson (1876) called attention to the fact that if solutions of copper were electrolysed in the presence of other metals, the latter greatly influenced the separation of the former. For example, with copper and antimony, the deposition of the copper was always incomplete when the antimony equaled one-fourth to two-thirds the quantity of the former. Notwithstanding, a complete separation of the two metals can be effected when the quantity of the antimony is small. A somewhat similar behavior was noticed with other metals. The deposition of cadmium, zinc, cobalt and nickel was apparently not satisfactory.

Lecoq de Boisbaudran (1877) electrolysed the potassium hydroxide solution of the metal gallium, using six Bunsen elements with 20–30 c.c. of the concentrated liquid. The deposited metal was readily detached when the negative electrode was immersed in *cold* water, and bent slightly.

The unpromising behavior of zinc solutions, observed by Wrightson, was fortunately overcome by

Parodi and Mascazzini (1877), who employed a solution of the sulphate, to which was added an excess of ammonium acetate. Lead was also deposited in a compact form from an alkaline tartrate solution of this metal in the presence of an alkaline acetate.

After Luckow's experiments upon manganese, little attention appears to have been given this metal until Riche (1878) published his results. While confirming the observations of Luckow, he discovered that manganese was not only completely precipitated from the solution of its sulphate, but also from that of the nitrate, thus rendering possible an electrolytic separation of manganese from copper, nickel, cobalt, zinc, magnesium, the alkaline earth and the alkali metals. Riche recommended that the deposited dioxide be carefully dried, converted by ignition into the protosesquioxide and weighed as such. According to this chemist, the one-millionth of a gram of manganese, when exposed to the action of the current, gave a distinct rose-red color, perceptible even when diluted tenfold.

In zinc depositions Riche gave preference to a solution of zinc-ammonium acetate containing free acetic acid.

Luckow was the first to mention that the current caused mercury to separate in a metallic form, from acid solutions, upon the negative electrode. F. W. Clarke (1878) used a mercuric chloride solution, feebly acidulated with sulphuric acid, for this purpose.

The deposition was made in a platinum dish, using six Bunsen cells. Mercurous chloride was at first precipitated, but it was gradually reduced to the metallic form. J. B. Hannay (1873) had previously recommended precipitating this metal from solutions of mercuric sulphate, but gave no results.

Clarke, also, gave some attention to cadmium; his results, however, were not satisfactory. A few months later the writer (1878) succeeded in depositing cadmium completely and in a very compact form from solutions of its acetate. Upon this behavior Yver (1880) based his separation of cadmium from zinc. Furthermore, the writer found (1880) that the deposition of cadmium could be made from solutions of its sulphate, contrary to an earlier observation of Wrightson. At the same time copper was completely separated from cadmium by electrolysing their solution in the presence of free nitric acid.

A very successful determination of both zinc and cadmium was published by Beilstein and Jawein in 1879. They employed for this purpose solutions of the double cyanides.

Heinrich Fresenius and Bergmann (1880) found that the electrolysis of nickel and cobalt solutions succeeded best in the presence of an excess of free ammonia and ammonium sulphate.

Their experience with silver demonstrated that the best results could be obtained with solutions containing free nitric acid, and by the employment of weak currents.

The writer showed (1880) that if uranium acetate solutions were electrolysed the uranium was completely precipitated as a hydrated protosesquioxide; and further, that molybdenum could be deposited as hydrated sesquioxide from warm solutions of ammonium molybdate in the presence of free ammonia. Very promising indications were obtained with salts of tungsten, vanadium and cerium.

In a more recent (1880) communication from Luckow, to whom we are indebted for much that is valuable in electrolysis, is given a full description of his observations in this field of analysis, from which the following condensed account is taken. While it relates more particularly to the qualitative behavior of various compounds, its importance demands careful study.

When the current is conducted through an acid solution of potassium chromate the chromic acid is reduced to oxide, whereas, if the solution of the oxide in caustic potash be subjected to a like treatment potassium chromate is produced. Arsenic and arsenious acid behave similarly. The same is true also of the soluble ferro- and ferri-cyanides and nitric acid. In the presence of sulphuric acid, ferric and uranic oxides are reduced to lower states of oxidation. Sulphates result in the electrolysis of the alkaline sulphites, hyposulphites and sulphides, and carbonates from the alkaline organic salts. In short, the current has a reducing action in acid solutions, and the opposite effect in those that are alkaline. In the electrolysis of solutions of hydrogen chloride, bromide, iodide, cyanide, ferro- and ferri-cyanide and sulphide, the hydrogen separates at the electro-negative pole, and the electro-negative constituents at the positive electrode. Cyanogen sustains a more thorough decomposition, the final products being carbon dioxide and ammonia. In the electrolysis of ferro- and ferri-cyanogen, Prussian blue separates at the positive electrode. In dilute chloride solutions hypochlorous acid is the only product, whereas chlorine is also present in concentrated solutions. In alkaline chloride solutions chlorates are produced as soon as the liquid becomes alkaline. In the iodides and bromides iodine and bromine separate at the positive electrode, while bromates and iodates are formed when metals of the first two groups are present. Potassium cyanide is converted into potassium and ammonium carbonates. Concentrated nitric acid is reduced to nitrous acid; however, when its specific gravity equals 1.2, this does not occur, at least not when a feeble current is used. Dilute nitric acid alone, or even in the presence of sulphuric acid, is not reduced to ammonia. If, however, dilute nitric acid be present in a copper sulphate solution undergoing electrolysis, copper will separate upon the negative electrode and ammonium sulphate will be formed. Solutions of nitrates, containing sulphuric acid, behave analogously. Phosphoric acid sustains no change. Silicic acid separates as a white mass, and boric acid, in crystals uniting to arborescent groups, at the positive electrode.

In the Ber. d. d. chem. Gesellschaft for 1881 (Vol. 14, 1622), Classen and v. Reiss presented the first of a series of papers upon electrolytic subjects, which continued through subsequent issues of this publication. Their early work was devoted to the precipitation of metals from solutions of their double oxalates. They also elaborated excellent methods for antimony and tin. Many very serviceable forms of apparatus, intended for electrolytic work, were devised and described by them, and it must be conceded that through the activity of the Aachen School electrolysis acquired more importance in the eyes of the chemical public than it ever before possessed. The details of the more important methods proposed by Classen and his co-laborers will receive due mention under the respective metals.

At the same time with and quite independently of Classen, Reinhardt and Ihle proposed the double oxalates for the estimation of zinc electrolytically; and in this connection it may not be improper to mention that as early as 1879, two years prior to the publication of Classen's first communication, Parodi and Mascazzini (Gazetta chimica italiana, Vol. 8) announced that antimony and iron could be deposited completely and in compact form by electrolysing the solutions of the sulpho-salts of the former and the chloride of the lattter in the presence of acid ammonium oxalate.

In 1883, Gibbs recommended placing solutions of mercury, tin and cobalt in a beaker glass, on the bottom of which was placed a layer of mercury, which served as the negative electrode. Knowing the combined weight of the beaker and mercury, the increased weight, after precipitation and removal of the liquid, will give the quantity of metal under examination. This method is not applicable in the case of antimony and arsenic.

Three years later (1886) Luckow recommended a very similar procedure for the estimation of zinc.

Moore (1886) also published new data upon the estimation of iron, cobalt, nickel, manganese, etc., full notice of which will appear under these metals.

The most recent publications relating to electrolysis are those of Brand, who succeeded in effecting separations by utilizing solutions of the pyrophosphates of different metals, and those of Smith and Frankel, who have made an extended study of the double cyanides, and found thereby a number of very convenient methods of separation heretofore unrecorded. The results are given in detail in the following pages.

The preceding paragraphs give a brief outline of what has been accomplished in the field of analysis by electrolysis; for further information consult the following

LITERATURE.—Jahrb., 1850, 602; C. r., **45**, 449; Jr. f. pkt. Ch., **73**, 79; Chem. Soc. Quart. Journ., **13**, 12; Jahrb., 1862, 610; Ann., **124**, 131; C. r., **55**, 18; Ann., **146**, 375; Z. f. a. Ch., **3**, 334; Ding. p. Jr. (1865), 231; Z. f. a. Ch., **8**, 23; **11**, 1, 9; **13**, 183; Am. Jr. Sc. and Ar. (3d ser.), **6**, 255; Z. f. a. Ch., **15**, 297; Ber., **10**, 1098; Annales de Ch. et de Phy., 1878; Am. Jr. Sc. and Ar., **16**, 200; Am. Phil. Soc. Pr., 1878; Z. f. a. Ch., **15**, 303; Am. Ch. Jr., **2**, 41; Berg-Hütt. Z., **37**, 41; Z. f. a. Ch., **19**, 1, 314, 324; Am. Ch. Jr., **1**, 341; B. s. Ch. Paris, **34**, 18; Ber., **12**, 1446; **14**, 1622, 2771; **17**, 1611, 2467, 2931; **18**, 168, 1104, 1787; **19**, 323; **21**, 359, 2892, 2900; Jr. f. pkt. Ch., **24**, 193; Z. f. a. Ch., **18**, 588; **22**, 558; **25**, 113; Chem. News, **28**, 581; **53**, 209. And the following will be found worthy of careful study: Ann., **36**, 32; **94**, 1; Z. f. a. Ch., **19**, 1; Berg-Hütt. Z., **42**, 377; Z. f. a. Ch., **22**, 485.

SPECIAL PART.

1. DETERMINATION OF THE DIFFERENT METALS.

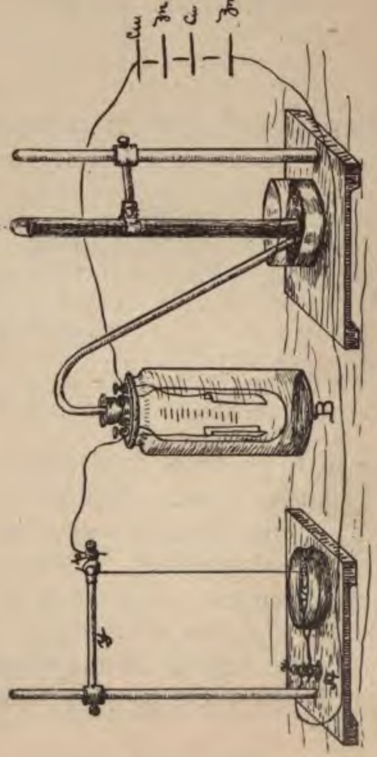
COPPER.

LITERATURE.—**Gibbs**, Z. f. a. Ch., **3**, 334; **Boisbaudran**, B. s. Ch., Paris, **1867**, p. 468; **Merrick**, Am. Ch., **2**, 136; **Wrightson**, Z. f. a Ch., **15**, 299; **Herpin**, Z. f. a. Ch., **15**, 335; Moniteur Scientifique [3 ser.], **5**, 41; **Ohl**, Z. f. a. Ch., **18**, 523; **Classen**, Ber., **14**, 1622, 1627; **Classen and v. Reiss**, Z. f. a. Ch., **24**, 246; **25**, 113; **Riché**, Z. f. a. Ch., **21**, 116; **Makintosh**, Am. Ch. Jr., **3**, 354; **Rüdorff**, Ber., **21**, 3050; **Luckow**, Z. f. a. Ch., **8**, 23.

Dissolve 19.6 grams of pure copper sulphate in water, and dilute to 1 litre. Place 50 c.c. of this solution (= 0.25 gram of metallic copper) in a *clean* platinum dish, previously weighed. Connect the dish with a battery, whose current is sufficiently strong to effect the complete precipitation of the copper in the course of ten or twelve hours. The apparatus may be arranged as in the accompanying sketch (Fig. 16), page 48.

A is an ordinary filter stand, upon the base of which is fixed a binding-post, *x*, to which is attached a heavy copper ring for the support of the platinum vessel. It

FIG. 16.



is in connection with the negative electrode of the battery. The arm, y, has been shortened, and at its extremity there is a second binding-screw, p; the latter holds the positive pole (a heavy platinum wire bent into a flat spiral at its lower end), and the copper wire from the anode of the battery (the copper plate in a "Crowfoot" cell). It will be noticed that the current passes through the vessel, B (a Bunsen voltameter), in which acidulated water is undergoing decomposition, the resulting gases being collected in d. Their volume serves to measure the strength of the acting current. Copper is very readily precipitated from solutions containing free nitric or sulphuric acid. Hydrochloric acid should never be present.

Having arranged the apparatus as just described, add 9–10 drops of concentrated nitric acid to the solution of the electrolyte; cover the vessel with a perforated watch crystal during the decomposition. To ascertain when the metal has been completely precipitated, add water to the dish; this will expose a clean, platinum surface, and if in the course of half an hour no copper appears upon it, the deposition may be considered as finished. Or, a drop of the liquid may be removed, and brought in contact with a drop of ammonium hydroxide or hydrogen sulphide, when, if a blue coloration or black precipitate is not produced, the deposition can be considered ended.

As the precipitation has been made in an acid solution, the current should not be interrupted until the

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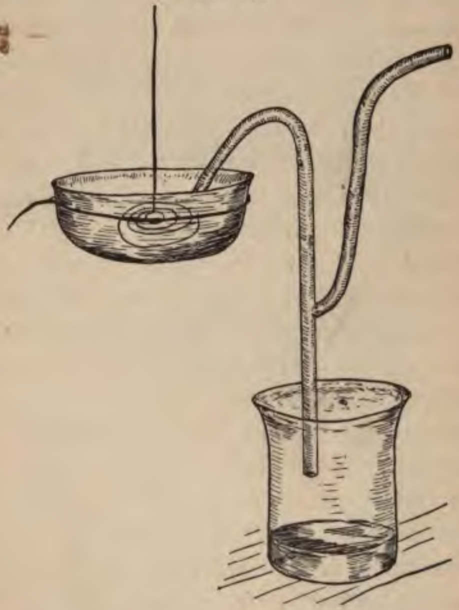
acid liquid has been removed, for in many cases the brief period during which the acid can act upon the metal will be sufficient to cause some of the latter to pass into solution. To obviate this, siphon off the acid liquid. The sketch (Fig. 17) shows how this can be done. A rubber tube of small diameter may be substituted for the glass siphon. As the acidulated water is conveyed away by the latter, pour distilled

FIG 17.



water into the dish. Empty the platinum dish twice in this way; the current can then be interrupted without loss of copper. Finally, disconnect the dish, wash the deposit with hot water and then with alcohol. Dry the precipitated copper at a temperature not exceeding 100° C.; an air-bath, an asbestos plate, or warm iron plate will answer for this purpose. Do not weigh the dish until it is perfectly cold, and has attained the temperature of the balance-room.

In the ordinary precipitations of copper from dilute nitric or sulphuric acid solution a current, giving 0.3–0.5 c.c. oxy-hydrogen gas (electrolytic gas) per minute, will be amply sufficient. The deposition can also be made in a platinum crucible, or the copper can be precipitated upon the exterior surface of the same. This is sometimes convenient. Place the liquid undergoing electrolysis in a beaker glass (capacity 100–250 c.c.), and suspend the crucible in it (Fig. 18); supporting it there by a tight-fitting cork, through which passes a stout copper wire, *w*, in connection with the negative electrode of a battery. The positive electrode is a platinum plate projecting into the liquid. The end of the decomposition may be learned by pressing down upon *w*, or by adding water to the solution in the beaker. No further appearance of copper on the newly exposed platinum indicates the end of the precipitation. Raise the crucible from the liquid, wash the copper with water, then detach the vessel carefully from the cork, and dry as already directed.

Instead of using either of the suggestions first offered, substitute the apparatus of Richè (Fig. 19) if convenient. This consists in suspending a crucible within a crucible. The sides of the inner vessel are perforated so that the liquid will maintain uniform concentration. It is practically the same as the device just described above.

FIG. 18.

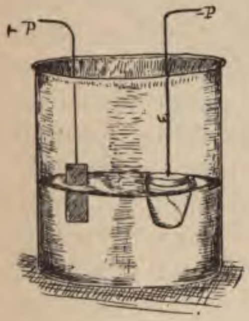
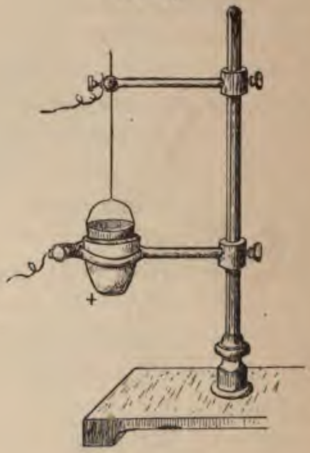
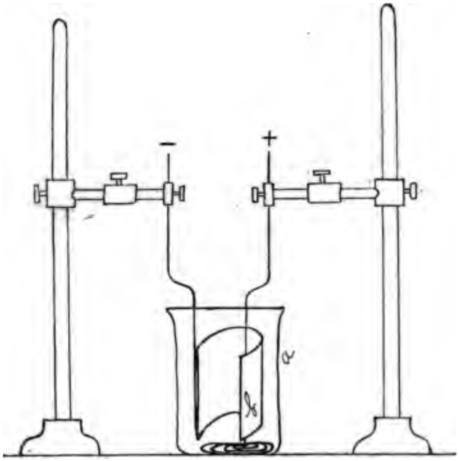


FIG. 19.



Copper can also be precipitated from the solution of ammonium-copper oxalate. To this end the copper solution (sulphate or chloride) is treated with an excess of a saturated solution of ammonium oxalate, care being taken that the entire volume does not exceed 170–200 c.c. A current liberating 0.1–0.2 c.c. oxy-hydrogen gas per minute will answer for the deposition, which will require about twelve hours. If the double oxalate solution be heated to 70°, and held at that temperature, the decomposition will be finished in five hours at the most. Use ferrocyanide of potassium to learn whether all the metal has been precipitated. Wash and dry as already instructed.

FIG. 20.



Rüdorff obtained excellent results with the following conditions: 0.1–0.3 gram of metallic copper in 100 c.c. water, to which were added 2–3 grams of potassium or ammonium nitrate, and 10 c.c. of ammonium hydroxide. A current giving 0.5 c.c. oxy-hydrogen gas per minute will throw out the copper from this solution.

Moore advises dissolving the recently precipitated copper sulphide, obtained in the ordinary course of analysis, in potassium cyanide; and, after the addition of an excess of ammonium carbonate, electrolyses the warm (70°) solution.

In the analysis of commercial copper Luckow employed the apparatus pictured in Fig. 20. The beaker (*a*) contains the electrolyte, and the metal is precipitated upon the cylinder of platinum (*b*). It is a very satisfactory device for almost any kind of electrolytic work.

Foote (Am. Ch. Jr., **6**, 333) has also described a very excellent improvement in the apparatus intended for the electrolytic precipitation of copper.

CADMIUM.

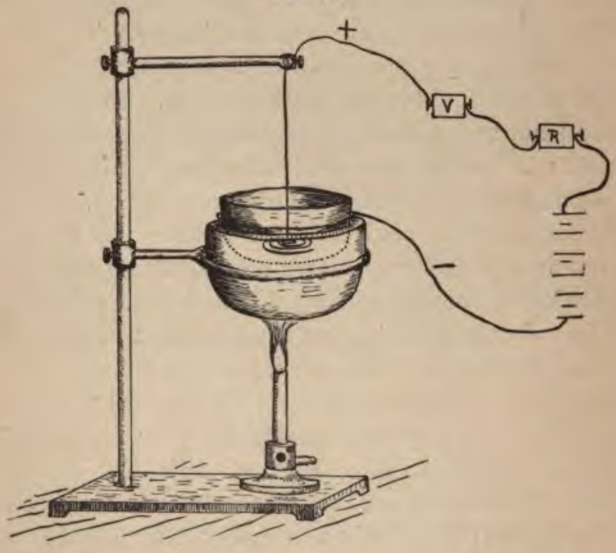
LITERATURE.—Ber., **11**, 2048; Smith, Am. Phil. Soc. Pr., 1878; Clarke, Z. f. a. Ch., **18**, 104; Beilstein and Jawein, Ber., **12**, 759; Smith, Am. Ch. Jr., **2**, 42; Luckow, Z. f. a. Ch., **19**, 16; Wrightson, Z. f. a. Ch., **15**, 303; Classen and v. Reiss, Ber., **14**, 1628.

Cadmium can be determined electrolytically as readily as copper. Prepare a solution of the chloride or sulphate of definite strength. Remove 50 c.c. to a suitable, weighed platinum vessel. Add one gram of pure potassium cyanide; dilute with water to 150–200 c.c., and then connect with five or six "Crowfoot" cells in the same manner as directed under copper. Introduce the voltameter as there indicated. It is well to commence the decomposition in the evening, and by morning the metal will be fully deposited. A current yielding 0.3 c.c. electrolytic gas per minute will precipitate 0.2 gram metal in this time. To ascertain whether the precipitation is complete, raise the level of the liquid in the platinum dish. In washing, it will not be necessary to siphon off the supernatant liquid; it can be poured off, after interruption of the current, without loss of metal from re-solution. Wash the deposit with cold and hot water. Dry upon a warm iron plate (temperature not exceeding 100° C.).

Cadmium may also be precipitated from a solution of its sulphate containing a small amount of free sulphuric acid (2 c.c. H_2SO_4, sp. gr. 1.09 for 0.1 gram cadmium). When operating with a solution of this character, use a current generating 5 c.c. electrolytic gas per minute. Two Bunsen cells will answer, although it may be necessary to reduce the current to some degree; this can be accomplished by introducing one of the resistances described on pages 26 and 27. Arrange the apparatus as under copper. The precipitation takes place at the ordinary temperature.

Cadmium can also be deposited quite readily, and in a crystalline form, from its acetate solution. In this case the liquid, containing an excess of free acetic acid, is heated to 70–80° during the decomposition. The apparatus can be arranged as in Fig. 21. The platinum dish is placed in a water bath, and the current made to pass through R (resistance frame) and V (voltameter). An asbestos plate may be substituted for the water bath. The current should give 1½–2 c.c. of oxy-hydrogen gas per minute. This will insure the precipitation of 0.12–0.15 gram of cadmium in five to six hours. When the precipitation is completed, detach the dish, wash the deposited metal first with

FIG. 21.



warm water, then with absolute alcohol, and finally with ether. Dry upon a moderately warm plate.

If desired, the metal can also be precipitated from the solution of the double oxalate of ammonium and cadmium (*see* Copper).

In the usual course of gravimetric analysis cadmium is obtained as sulphide. To prepare it for electrolysis dissolve the same in nitric acid, and after expelling the excess of the latter, add a small amount of potassium hydroxide (sufficient to precipitate the cadmium), and follow this with an excess of potassium cyanide (1 to 2 grams). Proceed further as already directed.

MERCURY.

LITERATURE.—Ber., **6**, 270; Clarke, Am. Jr. Sc. and Ar., **16**, 200; Classen and Ludwig, Ber., **19**, 323; Hoskinson, Am. Ch. Jr., **8**, 209; Smith and Knerr, *ibid.;* Smith and Frankel, Am. Ch. Jr., **11**, 264.

In preparing solutions for experimental purposes, use either mercuric nitrate or chloride. A current equivalent to 0.5–1.0 c.c. electrolytic gas per minute will precipitate 0.3 gram of mercury from such solutions (add a slight amount of free nitric acid) in twelve hours. The deposit will be drop-like in appearance. Even in the presence of considerable free nitric acid it has been found that a current of 4 c.c. electrolytic gas per minute will suffice to precipitate as much as 0.10 gram of metal in 30 to 45 minutes. In such cases the acid liquid must be removed before the interruption of the current occurs.

A mercuric chloride solution, feebly acidulated with sulphuric acid, gradually yields its metal to a current, giving 5–6 c.c. oxy-hydrogen gas per minute. Always wash the deposited metal with cold water.

From experiments made in this laboratory the writer prefers and would especially recommend solutions of the double cyanide of mercury and potassium for the electrolytic deposition of mercury. A current of 0.2 c.c electrolytic gas per minute will precipitate from 0.10–0.20 gram of metal in twelve hours. This procedure requires no further attention after it is once set in operation. The deposit is always compact, and gray in color. Use water only in washing it, for alcohol seems to detach some of the metallic film. The quantity of alkaline cyanide present may vary from 0.26–2.6 grams (KCN) for every gram of mercury.

In general analysis mercury is frequently obtained as sulphide. Its determination in this form requires time and exceeding care. As a substitute for this the writer would advise the solution of the sulphide in acid, and after neutralizing the excess of the latter with caustic alkali, add an excess of pure potassium cyanide, and electrolyse as above indicated. It is best to use a platinum dish as the negative electrode, and a platinum spiral (p. 49) for the anode. Dry the deposit on a moderately warm plate, or over sulphuric acid. "Crowfoot" cells are well adapted for decompositions of this kind.

BISMUTH.

LITERATURE.—Luckow, Z. f. a. Ch., **19**, 16; Classen and v. Reiss, Ber., **14**, 1622; Thomas and Smith, Am. Ch. Jr., **5**, 114; Moore, Ch. News, **53**, 209; Smith and Knerr, Am. Ch. Jr., **8**, 206; Schucht, Z. f. a. Ch., **22**, 492; Eliasberg, Ber., **19**, 326; Brand, Z. f. a. Ch., **28**, 596.

Prepare a solution of definite value as directed under the preceding metals. To a portion of it add an excess of a cold ammonium oxalate solution, and act upon the mixture with a current of 0.10 c.c. oxyhydrogen gas per minute. Those who have employed this method find that the deposit is not very adherent, and great care must be taken to expose as large a platinum surface as possible. If metallic particles do separate, collect them upon a small filter and weigh alone.

Eliasberg advises bringing the solution of the metal into a weighed platinum dish, and then adding 10 c.c. of a potassium oxalate solution (1 : 3). Heat is applied, and solid ammonium oxalate is introduced until complete solution ensues. Dilute to 170–180 c.c., and warm to 70–80° C., while the current acts. The latter should be so feeble that the liberation of gas in the voltameter is scarcely perceptible. In sixteen hours the greater portion of the metal will have separated, and then oxalic acid is added to distinct acid reaction. As soon as the metal is fully precipitated, interrupt the current and wash the deposit with water. Take special pains in drying, so that the metal does not oxidize.

Experiments made in this laboratory demonstrate that by electrolysing the sulphate, an alkaline citrate solution, or one containing free citric acid, the bismuth will be rapidly and completely precipitated. In some cases the deposits were made in small platinum crucibles, while others were thrown upon the exterior surface of the crucibles arranged as under Copper. If peroxide should separate upon the anode in the electrolysis of citrate or sulphate solutions of bismuth, it will disappear before the decomposition is fully ended. Heat is not required. The best results were obtained with solutions of the sulphate, containing free sulphuric acid. For example: 0.1542 gram of bismuth, as sulphate, 3 c.c. sulphuric acid (1.09 sp. gr.), and 150 c.c. of water, required a current giving 3 c.c. oxyhydrogen gas per minute, for a period of three hours, to effect the complete separation of the metal. The latter was quite compact and offered no difficulty in washing with water and alcohol. An air-bath was used for drying purposes.

Moore recommends the following method: add sufficient tartaric acid to the bismuth solution to prevent the precipitation of a basic salt, then, after rendering the solution slightly alkaline with ammonium hydroxide, add a considerable excess of glacial phosphoric acid, so that the solution has a strong acid reaction. The current should give 0.33–0.50 c.c. electrolytic gas per minute, at first, but this must be increased at last to 7.5 c.c. per minute. The deposit at the beginning of the deposition is loose, but gradually becomes hard and compact.

Brand's recommendation consists in adding to a somewhat dilute acid solution of bismuth from four to five times as much sodium pyrophosphate as will be necessary to form the double salt. Ammonium carbonate is then carefully introduced until the reaction of the liquid is distinctly alkaline, when 3–5 grams of ammonium oxalate are added. The total dilution should be about 200 c.c. The electrolysis is commenced with a current giving 0.1–1.0 c.c. electrolytic gas per minute, although toward the close it will be necessary to increase the same to 2–3 c.c. per minute. By following these instructions 0.2500 gram of bismuth can be precipitated in twelve hours. When considerable quantity of metal is present in solution a feeble current should be used at first. If the peroxide appears upon the anode in the course of the decomposition, redissolve it in a few drops of a concentrated solution of oxalic acid. However, this should not be done until there is no further separation of metal upon the cathode. The final reduction is ascertained by testing with hydrogen sulphide. The metal is said to sustain a superficial oxidation, hence it is converted into oxide and weighed as such.

LEAD.

LITERATURE.—Luckow, Z. f. a. Ch., **19**, 215; Riché, Ann. de Chim. et de Phys. [5 ser.], **13**, 508; Z. f. a. Ch., **21**, 117; Classen, *ibid.*, 257; Hampe, Z. f. a. Ch., **13**, 183; May, Am. Jr. Sc. and Ar. [3 ser.], **6**, 255, also Z. f. a. Ch., **14**, 347; Parodi and Mascazzini, Ber., **10**, 1098; Z. f. a. Ch., **16**, 469; **18**, 588; Riché, Z. f. a. Ch., **17**, 219; Schucht, Z. f. a. Ch., **21**, 488; Tenney, Am. Ch. Jr., **5**, 413; Smith, Am. Phil. Soc. Pr., **24**, 428.

The metal may be obtained by electrolysing solutions of the double oxalate (*see* Copper and Cadmium), the acetate, the oxide in sodium hydroxide, or the phosphate dissolved in the latter reagent. A current of 0.1–0.2 c.c. electrolytic gas per minute, is sufficient for this purpose. While the metal separates well from either one of these solutions, difficulty is experienced in drying the deposit, for the moist metal almost invariably suffers a partial oxidation, thus rendering the results high. The deposit can be dried, without oxidation, in an atmosphere of hydrogen, but for the inexperienced operator this procedure offers little satisfaction. It is, therefore, better to utilize the tendency of lead to separate, from acid solutions, as the dioxide. For trial purposes make up a definite volume of lead nitrate. Electrolyse several portions (= 0.1 gram lead each) in a platinum dish connected *with the anode* of a battery, giving 0.1–0.2 c.c. electrolytic gas per minute. In order that the lead may be precipitated wholly as dioxide upon the positive electrode and none in metallic form upon the cathode, it is necessary that the solution being analyzed should contain from ten to twenty per cent. of free nitric acid. This quantity of acid is required when lead alone is present in solution. In the presence of other metals the complete deposition of the lead as dioxide occurs with even less acid (eight per cent.). At the end of the precipitation siphon off the acid liquid, and wash in the dish, then dry the deposit at 110° C., and weigh. Reference to the literature shows that May preferred, after drying the deposit, to carefully ignite it and finally weigh as lead oxide (PbO). This deportment of lead affords an excellent method by which to separate it from other metals, *e.g.*, mercury, copper, cadmium, silver, and all those soluble in nitric acid, or those which, in a nitric acid solution, are deposited upon the electronegative pole of a battery.

The analysis of an alloy of lead, bismuth and copper can be most satisfactorily made by employing electrolytic methods (*see* Separations).

SILVER.

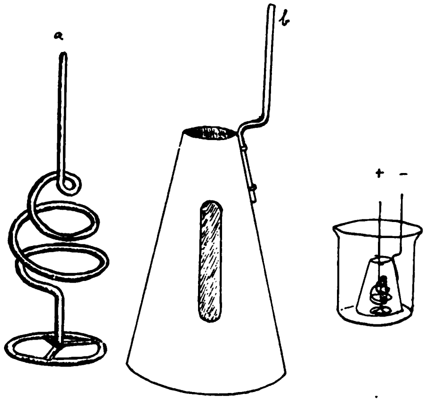
LITERATURE.—Luckow, Ding. p. Jr., **178**, 43, Z. f. a. Ch., **19**, 15; Fresenius and Bergmann, Z. f. a. Ch., **19**, 324; Krutwig, Ber., **15**, 1267; Schucht, Z. f. a. Ch., **22**, 417; Kinnicutt, Am. Ch. Jr., **4**, 22.

The experiments of Luckow showed that this metal could be deposited from solutions containing as high as eight to ten per cent. of free nitric acid. The deposit was spongy, and there was a simultaneous deposition of silver peroxide at the anode. This was, however, prevented by adding to the solution some glycerol, lactic or tartaric acid. A voluminous mass was also obtained from silver solutions, containing an excess of ammonium hydroxide or carbonate, and peroxide appeared at the same time upon the anode.

Fresenius and Bergmann, who have given the electrolysis of acid solutions of silver particular study, observed that the tendency of the metal to sponginess is most marked when the electrolyte is concentrated, and acted upon by a strong current. In a dilute liquid, the current being feeble, the deposit was compact and metallic in appearance (free acid should be present). From neutral solutions, although very dilute, the metal is separated in a flocculent condition by the feeblest currents. Therefore, to obtain results that would answer for quantitative analysis, the following conditions were adopted: The total dilution of the solution was 200 c.c.; in this there was 0.03 gram–.04 gram silver, and 3–6 grams of free nitric acid. The poles were separated about 1 cm. from each other, while the current gave 100–150 c.c. electrolytic gas per hour.

In the experiments of Fresenius and Bergmann, apparatus similar to that in Fig. 22 was employed. It has some decided advantages. Both spiral (*a*) and cone (*b*) are constructed of platinum. The metallic deposition, it will be understood, occurs upon the cone, the sides of which are perforated, so that a uniform concentration of liquid is preserved throughout the decomposition. When liquid electrolytes contain much iron, it is essential that the oxygen liberated within the cone should be equally distributed over its outer surface. This is made possible through openings. The shape of the cone also prevents loss from the bursting of the bubbles, arising from the platinum spiral in connection with the anode.

FIG 22.



Krutwig advises adding a large excess of ammonium sulphate to the silver solution, previously made alkaline with ammonium hydroxide, and employs a current giving 150 c.c. electrolytic gas per hour, but after half an hour the latter is increased to 300 c.c. of gas per hour. In this way, 0.1 gram of silver is precipitated in two hours.

The writer's experience has chiefly been with solutions of silver containing an excess of alkaline cyanide (1 gram KCN for 0.2–0.3 gram silver). With these peroxide separation does not occur, and a very weak current will precipitate 0.15–0.20 gram metal in ten hours from a cold solution. The precipitation can be made either in a platinum dish or crucible as cathode.

Chlorine, bromine and iodine can be indirectly estimated electrolytically by first precipitating them as silver salts, then dissolving the latter in potassium cyanide, and exposing the resulting solution to the action of a current from three to four "Crowfoot" cells.

Luckow reduced silver chloride by placing it in a platinum dish, serving as the negative electrode, covered it with dilute sulphuric or acetic acid, and allowed the positive electrode to project into the solution. Four Meidinger cells were strong enough to reduce 0.1 gram silver chloride in ten minutes. The deposit, while spongy, was adherent. It was washed with water and then thoroughly dried to insure the absence of any acid. (See the reference to Kinnicutt's experiments; also Prescott and Dunn, Jr. An. Ch., **3**, 373.)

ZINC.

LITERATURE.—Wrightson, Z. f. a. Ch., **15**, 303; Parodi and Mascazzini, Ber., **10**, 1098, Z. f. a. Ch., **18**, 587; Riché, Z. f. a. Ch., **17**, 216; Beilstein and Jawein, Ber., **12**, 446, Z. f. a. Ch., **18**, 588; Riché, Z. f. a. Ch., **21**, 119; Reinhardt and Ihle, Jr. f. pkt. Ch., [N. F.], **24**, 193; Classen and v. Reiss, Ber., **14**, 1622; Gibbs, Z. f. a. Ch., **22**, 558; Luckow, Z. f. a. Ch., **25**, 113.

Much has been written upon the electrolytic estimation of zinc. The personal experience of the writer inclines him to give preference to the method suggested by Parodi and Mascazzini. They recommended that the metal be present in solution as sulphate; its quantity may vary from 0.1–0.25 gram. To it add 4 c.c. of a solution of ammonium acetate, 20 c.c. citric acid, and dilute to 200 c.c. with water. The electrodes are then introduced into the liquid, their distance apart being not more than a few millimetres. The precipitation can be made in a beaker glass, using a weighed platinum cone (Fig. 22) as the cathode. The current for this purpose should give 250–300 c.c. electrolytic gas per hour. When the precipitation of metal has ended, which may be ascertained by removing a small quantity of the liquid with a capillary tube and bringing it in contact with a drop of a solution of potassium ferrocyanide, remove the bulk of the liquid with a siphon. Wash the deposit with water and alcohol. There is no danger of oxidation during the drying process. It will be discovered on dissolving the precipitated zinc that a considerable quantity of the metal remains unattacked, but this can be removed by gently heating the residue with air contact, then fusing it with potassium bisulphate.

Beilstein and Jawein add sodium hydroxide to the solutions of zinc nitrate or sulphate, until a precipitate is produced, and dissolve it in potassium cyanide. The decomposition is carried out in a rather large beaker glass, the cathode being either the platinum cone already described (p. 65), or a rather large platinum crucible suspended from a cork (p. 52), perforated by a copper wire, touching the inner surface of the crucible. Four Bunsen cells (usual size) are sufficient for the precipitation. Wash the deposit as instructed above.

Reinhardt and Ihle have objected to nearly all the methods which have been proposed for the electrolytic estimation of zinc. They say of the Beilstein and Jawein method . . . . that the results are fairly good, ... but a strong current is necessary, otherwise the precipitation of the zinc is slow and incomplete, ... the positive pole diminishes in weight very appreciably, ... finally, working with potassium cyanide is very unpleasant. The writer's experience has proved that a current considerably less than that which Beilstein and Jawein first recommended will throw out all the zinc in the course of a night, and further that the anode is not appreciably affected. The method suggested by Reinhardt and Ihle is, however, very excellent and deserves trial by all interested in the electrolytic estimation of zinc. Its essential features, taken from their publication, are these: Mix the solution of zinc sulphate or chloride, neutral as possible, with an excess of neutral potassium oxalate, until the precipitate, which appears at first, redissolves. A current giving 90 c.c. electrolytic gas per hour will answer for complete precipitation.

The immediate decomposition of the zinc oxalate is into zinc and carbon dioxide (two molecules), and the potassium oxalate into carbon dioxide (two molecules) and potassium; the latter then reacts with the water, so that while an abundant liberation of hydrogen occurs at the cathode, the alkali simultaneously set free is converted into acid potassium carbonate by the carbon dioxide at the anode:—

$$ZnC_2O_4 + K_2C_2O_4 = \underset{\text{Cathode.}}{(Zn + 2KOH + H_2)} + \underset{\text{Anode.}}{4CO_2}.$$

$$2KOH + 2CO_2 = 2CO\left\langle\begin{matrix}OH\\OK\end{matrix}\right..$$

Therefore, just as long as zinc oxalate is being decomposed, considerable evolution of gas is noticeable at the positive electrode, and when this diminishes, and occasional bubbles escape, the decomposition is complete, and the deposition of metal may be considered finished.

Free oxalic acid, or any other acid, is not injurious if there is a sufficient quantity of potassium oxalate present. Nitric acid, however, free or combined, should be avoided; it gives rise to ammonium salts, which prevent the zinc from separating in a dense form. The acid potassium carbonate produced during the decomposition offers great resistance to the current; it is, therefore, advisable to add potassium sulphate to the solution to increase its conductivity. Reinhardt and Ihle recommend the following solutions for use in decompositions like that just described: 166 grams of potassium oxalate in 1 litre of water; 250 grams of potassium sulphate in 1 litre of water, and a solution of oxalic acid saturated at 15° C.

Experiments.—(1) 40 c.c. of a solution of zinc sulphate (= 0.1812 gram metallic zinc), to which were added 50 c.c. of potassium oxalate and 100 c.c. of potassium sulphate, were electrolysed with a current giving 109 c.c. of electrolytic gas per hour. After five hours the current was interrupted. The precipitated zinc weighed 0.1814 gram. (2) 2.1867 grams brass (containing tin, copper, lead and zinc) were dissolved in nitric acid and the tin determined in the usual gravimetric way. Its quantity was found to be 0.04 per cent. In the filtrate, containing nitric acid, lead and copper were determined simultaneously by electrolysis (the copper separated upon the cathode and the lead as dioxide upon the anode):—

$$\text{Found}\begin{cases} a\text{—}0.85\%\ \text{Pb and } 64.60\%\ \text{Cu.} \\ b\text{—}0.85\text{ `` `` `` } 64.62\text{ `` ``} \end{cases}$$

The acid liquid was siphoned off from the deposits, evaporated to dryness with sulphuric acid, neutralized with caustic potash, and then to this (100 c.c. in volume) solution were added 50 c.c. of a solution of potassium oxalate and 100 c.c. of a solution of potassium sulphate. The zinc found equaled 34.50 per cent.

When using this method employ a stout platinum wire, wound to a spiral at the one end, for the anode, and a platinum cone for the cathode. To avoid the peculiar spots which electrolytic zinc shows upon a platinum surface, it will be best to first coat the negative electrode with copper (5 grams). In dissolving the precipitated zinc, use rather dilute nitric acid. The copper layer will be but slightly attacked, and after washing and drying will serve for further depositions. Wash the zinc deposit with water, alcohol and ether; dry in a desiccator. Oxidation is liable to occur if an air bath be used for the drying.

Richè employs "a solution of the acetate with an excess of ammonium acetate, obtained by supersaturation with ammonia, and acidifying with acetic acid." This method affords good results, as may be seen from the following determination: 0.4736 gram of zinc sulphate was dissolved in 200 c.c. of water, to which were added three grams of sodium acetate and ten drops of ordinary acetic acid. The current gave 3 c.c. of electrolytic gas per minute. After two hours 0.1063 gram of metallic zinc was obtained, the required quantity being 0.1072 gram.

Moore seems to have obtained exceedingly satisfactory results by precipitating a solution of zinc sulphate with sodic phosphate, then adding an excess of ammonium carbonate, and after dissolving the precipitate in potassium cyanide, the solution was electrolysed at a temperature of 80° with a current giving 1000 c.c. electrolytic gas per hour. The metal was deposited upon a silver-plated electrode.

A very convenient stand for electrolytic work and suitable in the zinc depositions has been described by v. Malapert (Z. f. a. Ch., **26**, 56), and since conveniently modified by Herrick (Jr. An. Ch., **2**, 167).

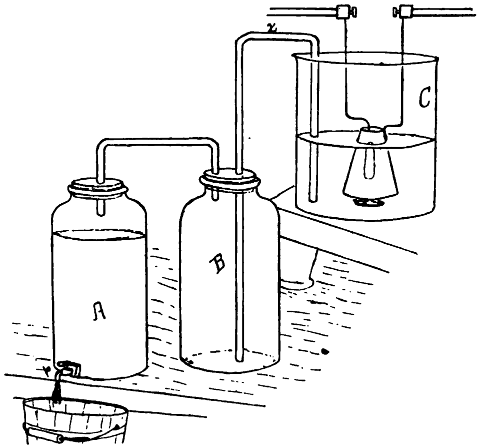
NICKEL AND COBALT.

LITERATURE.—Gibbs, Z. f. a. Ch., **3**, 336; Z. f. a. Ch., **11**, 10; **22**, 558; Merrick, Am Ch., **2**, 136; Wrightson, Z. f. a. Ch., **15**, 300, 303, 333; Schweder, Z. f. a. Ch., **16**, 344; Cheney and Richards, Am. Jr. Sc. and Ar. [3], **14**, 178; Ohl, Z. f. a. Ch., **18**, 523; Luckow, Z. f. a. Ch., **19**, 16; Bergmann and Fresenius, Z. f. a. Ch., **19**, 314; Richè, Z. f. a. Ch., **21**, 116, 119; Classen and v. Reis, Ber., **14**, 1622, 2771; Schucht, Z. f. a. Ch., **21**, 493; Kohn and Woodgate, Jour. Soc. Chem. Industry, **8**, 256.

These metals are precipitated from solutions of their double cyanides, double oxalates, and sulphates mixed with alkaline acetates, tartrates and citrates, or from ammoniacal solutions. The latter seem best adapted for nickel depositions, the presence of ammonium sulphate or sodium phosphate being favorable to the precipitation.

Fresenius and Bergmann, who have carried out a series of experiments with nickel and cobalt, give the following as satisfactory conditions: 50 c.c. nickel solution (= 0.1233 gram nickel), 100 c.c. ammonia (sp. gr. 0.96), 10 c.c. ammonium sulphate (305 grams of the salt in 1 litre of water), 100 c.c. of water; separation of the electrodes ½–⅓ cm.: time, four hours. Current, 300 c.c. electrolytic gas per hour. The nickel found was 0.1233 gram. Apparatus suitable for the decomposition just described is represented in Fig. 23. The metal is deposited upon the weighed platinum cone in the beaker glass, *C*. The vessel is covered

FIG. 23.



with a glass lid having suitable apertures for the positive and negative electrodes. As soon as the blue-colored liquid becomes colorless, an indication that the metal is completely precipitated, remove a few drops and test with a solution of potassium sulpho-carbonate. If the latter causes only a faint rose-red coloration the deposition of metal may be considered complete. It is not advisable to interrupt the current or to remove the cone from the electrolysed liquid until the latter has been replaced by water. This is effected by the vessels to the left of the figure: *A* is an aspirator, filled with water; *B* is air-tight and empty; *x* is a doubly bent tube extending to the bottom of *C*. Open *p* and the liquid in *C* is gradually transferred to *B*. Add fresh water in *C*. Ammonium chloride should not be present in the solution undergoing electrolysis.

The statements upon nickel also apply to cobalt. An experiment, taken from the article of Fresenius and Bergmann is here given as a guide in determining cobalt: 50 c.c. of cobalt sulphate (= 0.1286 gram cobalt), 100 c.c. of ammonia, 10 c.c. of ammonium sulphate, 100 c.c. water; current, 300 c.c. electrolytic gas per hour; separation of electrodes, ½–⅓ cm. Time, five hours. The deposited cobalt weighed 0.1286 gram.

Use potassium sulpho-carbonate to test when the metal is fully reduced; it gives a wine-yellow coloration with even the most dilute solutions of cobalt salts.

When too little ammonia is present in the electrolyte the results are bad; too much of this reagent retards the deposition of the cobalt.

When precipitating these metals from the solutions of their double oxalates, the conditions should be similar to those indicated under Iron (p. 78).

The writer has electrolysed cobalt compounds containing an excess of an alkaline acetate (*see* Zinc) with perfectly satisfactory results, and would recommend such solutions for this particular metal.

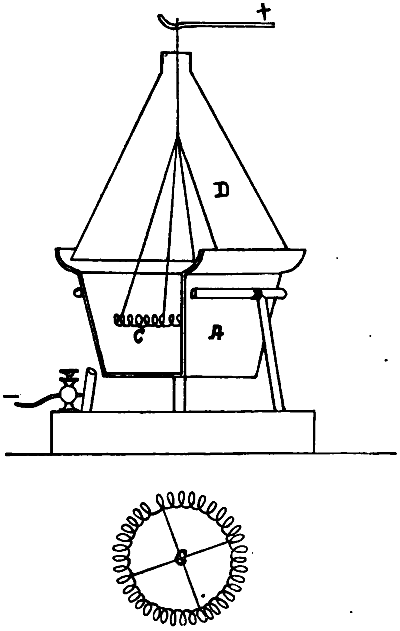
MANGANESE.

LITERATURE.—Z. f. a. Ch., 11, 14; Richè, Ann. de Chim. et de Phys. [5th ser.], 13, 508; Luckow, Z. f. a. Ch., 19, 17; Schucht, Z. f. a. Ch., 22, 493; Classen and v. Reiss, Ber., 14, 1622; Moore, Ch. News, 53, 209; Smith and Frankel, Jr. An. Ch., 3, 385; Ch. News, 60, 262; Brand, Z. f. a. Ch., 28, 581.

The electric current causes this metal, when in solution as chloride, nitrate or sulphate, to separate as the dioxide upon the anode (*see* Lead). In a solution of nitric acid, the hydrogen set free reduces the acid to oxides of nitrogen and, finally, to ammonia. Hence, when the liquid becomes alkaline or only slightly acid, peroxide will also separate upon the cathode; it will be necessary to remove this by means of a strip of paper, and ignite the same along with the greater bulk of dioxide, weighing all finally as Mn_3O_4. As long as manganese alone is present in the solution, this separation at both electrodes will not cause a serious result; but in electrolysing a nitric acid solution containing manganese, magnesium or aluminium, the results will be high. For this reason a solution of the sulphate, slightly acidulated with two to six drops of sulphuric acid, is preferable for electrolytic purposes. Richè advises connecting a platinum crucible or dish with the anode of a battery, warming the solution, during the deposition, upon a water-bath (70°–90°), and then electrolyses with a current generating 3 c.c. of oxy-hydrogen gas per minute. Arrange the apparatus as directed under Cadmium. As soon as the manganese has been fully precipitated as dioxide, the current is interrupted, the deposit washed with water, and should any of the dioxide become detached, it must be caught upon a small filter, then dried, ignited and weighed, together with the adherent dioxide, which is changed to Mn_3O_4 before weighing. In the presence of large quantities of iron, this precipitation is unsatisfactory; therefore, first remove the iron with barium carbonate. Tartaric, oxalic and lactic acids retard the formation of manganese dioxide. The same is true of phosphoric acid. Potassium sulphocyanide also prevents its formation, and, if added to solutions in which dioxide is already precipitated, it causes the same to redissolve.

The apparatus devised by Herpin (Fig. 24) can be well applied in the decomposition of manganese salts. It consists of a platinum dish, *A*, resting upon a tripod, *B*, in connection with the cathode of a battery. The upper portion of the dish is so constructed that it will support an inverted glass funnel, *D*. Any loss from the bursting of bubbles is prevented by this

FIG. 24.



means. The anode is a platinum spiral *C*. In estimating manganese it must not be forgotten to connect the dish with the anode of the battery employed for the decomposition.

IRON.

LITERATURE.—Wrightson, Z. f. a. Ch., **15**, 305; Parodi and Mascazzini, G. Ch. ital., **8**; also Z. f. a. Ch., **18**, 588; Luckow, Z. f. a. Ch., **19**, 18; Classen and v. Reiss, Ber., **14**, 1622; Moore, Ch. News, **53**, 209; Smith, Am. Ch. Jr., **10**, 330; Brand, Z. f. a. Chem., **28**, 581.

In the historical sketch p. 44, it was mentioned that Parodi and Mascazzini found that iron could be precipitated from solutions of its double oxalates. This suggestion has since been greatly elaborated by Classen, and by him applied to many other metals. Following the recommendation of this chemist the iron salt is placed in a weighed platinum dish connected with the cathode of a battery, and to this are added 1 – 3 c.c. of a solution of potassium oxalate (1 : 3), and 25 c.c. of water. 3 – 4 grams of ammonium oxalate are next introduced into this liquid and dissolved by the aid of heat, and the entire solution then diluted to 200 c.c., and electrolysed with a current generating 12 c.c. of electrolytic gas per minute. It is necessary to increase this toward the end of the reduction, to insure the complete deposition of the metal. Test the clear liquid, acidulated with hydrochloric acid, with potassium sulphocyanide. The solution should be hot (70°) during the decomposition. The deposited iron has a steel-gray color; it should be washed with water, alcohol and ether. Avoid the presence of chlorides and nitrates. By carefully complying with the conditions recommended by Classen good results are sure to follow. To show that persons with but little experience can obtain satisfactory results the two following determinations, made by a student, are given: A quantity of ferric ammonium sulphate (= 0.0814 gram iron) was dissolved in 200 c.c. of water, and to this were added eight grams of ammonium oxalate. The solution was heated to 80°, and in two hours, with a current of 15 c.c. electrolytic gas per minute, 0.0814 gram of iron was obtained. In a second experiment, the quantity of iron was doubled (= 0.1628 gram iron), while the ammonium oxalate was 11 grams, temperature 66° and the current 10 c.c. electrolytic gas per minute. The precipitated iron weighed 0.1619 gram instead of 0.1628.

The writer found the following procedure admirably suited for iron determinations: 10 c.c. iron solution (= 0.0300 gram metal), 20 c.c. sodium citrate (28 grams in ¼ litre) with a little free citric acid, then diluted with water to 150 c.c. Current, 12 c.c. electrolytic gas per minute. In four hours 0.0303 gram iron was precipitated from the cold solution. The deposit was washed as already directed. In several determinations aluminium and titanium were present with the iron, but the latter was precipitated free from the other two.

A third method, originated by Moore, advises that glacial phosphoric acid (15% acid) be added to the distinctly acid solution of ferric chloride or sulphate, until the yellow color fully disappears, then a large excess of ammonium carbonate added and gently warmed until the liquid becomes clear. On electrolysing the hot (70°) solution by a current equal to 1200 c. c. electrolytic gas per hour, the iron is rapidly and completely deposited at the rate of 0.75 gram per hour. The end of the decomposition is recognized by testing a portion of the solution with ammonium sulphide. Wash the deposit as already directed.

URANIUM.

LITERATURE.—Luckow, Z. f. a. Ch., 19, 18; Smith, Am. Ch. Jr., 1, 329.

For electrolytic purposes use the acetate or any of the salts to which an alkaline acetate has been added in large excess, together with a few drops of free acetic acid. The dish in which the deposition is made is placed upon a water-bath, and connected with the negative electrode of a battery giving 2–3 c.c. of electrolytic gas per minute (see Cadmium). Heat the liquid to 70° throughout the entire decomposition. The uranium separates as yellow uranic hydroxide upon the cathode; by the continued action of the current it changes to the black hydrated protosesquioxide. As soon as the solution becomes colorless, interrupt the current, and quickly pour the clear liquid upon a small filter, to catch any detached particles of oxide. Wash with a little acetic acid and boiling water; dry, ignite and weigh as $Ur_3O_4(Ur_3O_8)$. This method affords an excellent separation of uranium from the alkali and alkaline earth metals.

THALLIUM.

LITERATURE.—Schucht, Z. f. a. Ch., **22**, 241, 490; Neumann, Ber., **21**, 356.

This metal separates as sesquioxide, from acid solutions, upon the anode, while from ammoniacal liquids it is deposited partly as metal and partly as oxide. From oxalate solutions, and from its double cyanides it separates only as metal, when the current is feeble. However, difficulty is experienced in drying the deposit without having it oxidized. In this respect it is even more troublesome than lead. Neumann utilizes the current to separate the metal, dissolves the latter in acid and measures the liberated hydrogen; from its volume he calculates the quantity of thallium originally present. For suitable apparatus to carry out this method, consult the literature cited above.

PLATINUM, PALLADIUM, MOLYBDENUM, GOLD, ETC.

LITERATURE.—Luckow, Z. f. a. Ch., **19**, 13; Classen, Ber., **17**, 2467; Schucht, Z. f. a. Ch., **22**, 242; Smith, Am. Ch. Jr., **1**, 329; Hoskinson and Smith, *ibid.*, **1**, 90; Smith and Keller, Am. Ch. Jr., **12**, 252.

The solutions of platinum salts, slightly acidulated with sulphuric acid, and acted upon by a feeble current, give up the metal as a bright, dense deposit upon the dish, frequently so light as to be scarcely distinguished from the latter. In using platinum vessels for this purpose, first coat them with a rather thick layer of copper, upon which afterward deposit the metal. Wash the deposit with water and alcohol.

In ordinary gravimetric analysis, potassium is frequently estimated as potassio-platinum chloride, K_2PtCl_6. This operation requires time and care. Rather dissolve the double salt in water, slightly acidulate the solution with sulphuric acid, and electrolyse with one Bunsen cell. The deposit will be black and spongy if the current is too strong. From the quantity of platinum found calculate the potassium.

The following facts have been taken from Classen's article (*see* Literature): A platinic chloride solution, containing 0.6 gram platinum, was diluted to 200 c.c. with water and electrolysed. In five hours 0.4581 gram platinum had separated. When mixed with ammonium oxalate 0.0996 gram platinum was precipitated in two hours. From a solution, feebly acidulated with hydrochloric acid, four Meidinger cells precipitated 0.737 gram platinum in the course of twenty-four hours. On dissolving 0.5 gram ammonio-platinum chloride in 100 c.c. water and mixing with ammonium oxalate the current from *one* Bunsen cell precipitated 0.208 gram platinum in five hours. 0.6042 gram potassio-platinum chloride was dissolved in 150 c.c. of water, acidulated with thirty drops of dilute sulphuric acid (1 : 6), and in six hours gave 0.2017 gram platinum to the action of the current; 0.5015 gram of the same salt gave 0.0956 gram metal in two hours; while 0.4545 gram of the double chloride dissolved in 100 c. c. water, and not acidulated, gave 0.0688 gram platinum in three hours.

PALLADIUM can be deposited in the same manner as platinum. The use of a feeble current gives a bright metallic deposit; otherwise it is spongy.

It has been recently discovered, in this laboratory, that this metal can be rapidly and fully precipitated from ammoniacal solutions of palladammonium chloride, by a current liberating 0.7 c.c. electrolytic gas per minute. Palladammonium chloride, $Pd(NH_3Cl)_2$, is prepared by adding hydrochloric acid to an ammonium hydroxide solution of palladious chloride. To show the accuracy of this method several actual determinations are here introduced: (1) A quantity of the double salt (= 0.2228 gram palladium) was dissolved in ammonium hydroxide; to this solution were added 20–30 c.c. of the same reagent (sp. gr. 0.935), and 100 c.c. of water. A current, giving 0.9 c.c. electrolytic gas per minute, acted upon this mixture through the night, and deposited 0.2225 gram palladium. (2) In another experiment, with conditions similar to those just mentioned, excepting that the quantity of the palladammonium chloride was doubled, and the current reduced to 0.7 c.c. electrolytic gas per minute, the quantity of metal precipitated equaled 0.4462 gram instead of 0.4456. Oxide did not separate upon the anode. The deposit, when dry, showed the same appearance as is ordinarily observed with this metal in sheet form. It was washed with hot (70°) water, and dried in an air-bath at 110°–115°. It is best to deposit the palladium in platinum dishes previously coated with silver.

WHEN the electric current acts upon ammoniacal, or feebly acid solutions of ammonium molybdate, a beautiful iridescence appears; as the action continues this assumes a black color, and the deposit becomes more dense. It is the hydrated sesquioxide, which is precipitated; after washing with hot water it is dried, carefully ignited to molybdic acid, and weighed. The precipitation can take place in a platinum crucible, in connection with the cathode of a battery liberating 3–4 c.c. of electrolytic gas per minute. The temperature of the solution should not fall below 70°; its volume may vary from 25 c.c.–125 c.c. Three hours were required for the precipitation of 0.0329–0.1000 gram of oxide.

GOLD is best deposited from solutions of its double cyanides.

THE facts relating to the electrolytic behavior of vanadium, tungsten and osmium are, at the present writing, few in number and will not be given here.

TIN.

LITERATURE.—Luckow, Z. f. a. Ch., 19, 13; Classen and v. Reiss, Ber., 14, 1622; Gibbs, Ch. News, 42, 291; Classen, Ber., 17, 2467; 18, 1104.

Tin may be deposited either from a solution of its chloride, or from that of ammonium tin oxalate. It is advisable not to use potassium oxalate in the electrolysis, for then a basic salt is liable to separate upon the anode. Three to four grams of ammonium oxalate will be sufficient for the decomposition. The current should liberate 3 c.c. electrolytic gas per minute. When electrolysing acid tin solutions do not interrupt the current until the free acid is first removed; this is not necessary when operating with oxalate solutions.

Classen has published a great deal of very valuable information upon the electrolysis of this metal, and has discovered that a tin solution, containing an excess of ammonium sulphide, largely diluted with water, yields a quantitative deposition of the metal when exposed to the action of a current from two Bunsen cells. In dilute sodium or potassium sulphide solution the tin precipitation is incomplete, and whenever such conditions exist, the sodium or potassium salt must be converted into ammonium sulphide. To this end the liquid is mixed with about 25 grams of ammonium sulphate, free from iron, and the solution then carefully warmed in a covered vessel until the evolution of hydrogen sulphide ceases; after which the liquid is heated to incipient ebullition for fifteen minutes. Allow it to cool, dissolve any sodium sulphate which may have separated by the addition of water, and electrolyse with a current of 9–10 c.c. oxy-hydrogen gas per minute. The tin separates in a gray, dense layer. Wash it with water and alcohol. At times sulphur sets itself upon the tin deposit; this is difficult to remove, but can be detached, after washing the deposit with alcohol, by gently applying a linen handkerchief.

ANTIMONY.

LITERATURE.—Wrightson, Z. f. a. Ch., 15, 300; Parodi and Mascazzini, Z. f. a. Ch., 18, 588; Luckow, Z. f. a. Ch., 19, 13; Classen and v. Reiss, Ber., 14, 1622; 17, 2467; 18, 1104; Lecrenier, Chemiker Zeitung, 13, 1219; Chittenden, Pro. Conn. Acad. Sci., Vol. 8.

Antimony, when precipitated from a solution of its chloride, or from that of antimony potassium oxalate, does not adhere well to the cathode. It is deposited very slowly from a solution of potassio-antimony tartrate. Its deposition from a *cold* ammonium sulphide solution is satisfactory, but the use of this reagent for this purpose is not pleasant, especially when several analyses are being carried out simultaneously. For this reason potassium or sodium sulphide has been substituted. The alkaline sulphide used must not contain iron or alumina.

The antimony solution, mixed with sodium sulphide, is largely diluted with water. A more rapid reduction follows in consequence of the dilution. A current giving 2–3 c.c. of electrolytic gas per minute will precipitate 0.1 gram of antimony in four or five hours. To ascertain when all the metal is deposited incline the dish slightly, thus exposing a clean platinum surface. If this remains bright for half an hour the precipitation is finished. In separating antimony from the heavy metals, *e. g.*, lead, it happens that alkaline sulphides containing polysulphides are used, or are produced. To remove these Classen proposed adding to the antimony-polysulphide mixture, already in a weighed platinum dish, an ammoniacal solution of hydrogen peroxide, and warming the same until the liquid becomes colorless. When this is accomplished, even if a precipitate has been produced, add, after cooling, 10 c.c. of a concentrated solution of sodium monosulphide, and electrolyse with a current of 1.5–2 c.c. electrolytic gas per minute. Wash the deposit with water and alcohol.

Lecrenier writes as follows relative to the preceding method: The precipitation is all that one can desire, providing the solution of the sulpho-salt is absolutely free from polysulphides; otherwise, it is incomplete. The antimony sulphide, obtained in the ordinary course of analysis, always contains sulphur, and this must be eliminated. To remove the various inconveniences connected with the method add 50–75 c.c. of a 20 per cent. solution of sodium sulphite to the solution after the addition of the excess of sodium sulphide, then heat the liquid to complete decolorization; allow to cool, after which the current is conducted through the liquid. This can rise to 5 c.c. per minute without impairing the result; but it is not best, as the precipitated metal is then not very coherent. It is better to use a current giving not more than half of the above volume of electrolytic gas per minute. When the quantity of antimony does not exceed 0.2 gram the deposit will be adherent and free from sulphur; wash with water, alcohol and ether. Sulphur will separate upon the anode, despite the presence of an excess of sodium sulphite. This, however, does not affect the result.

ARSENIC.

LITERATURE.—Luckow, Z. f. a. Ch., 19, 14; Classen and v. Reiss, Ber., 14, 1622; Moore, Ch. News, 53, 209.

A successful method for the complete deposition of arsenic is not known. The current, acting upon the chloride, causes complete volatilization of the metal in the form of arsine. Its separation from oxalate solutions is incomplete; nor do the sulpho-salts answer for electrolytic purposes.

2. SEPARATION OF THE METALS.

Electrolysis, to be of value, must not only furnish the analyst with methods suitable for the complete deposition of metals, but it should, in addition, enable him to separate metallic mixtures. The data given in the preceding pages will serve for this purpose, but, as special treatment is required in some instances, a brief outline of a series of separations will be indicated.

COPPER.

We recall, first of all, that this metal can be deposited electrolytically from solutions in which free nitric acid is present (p. 51). This behavior renders the separation of copper from cadmium possible (Am. Ch. Jr., **2**, 42). Place the solution containing the two metals in a beaker glass of 200 c. c. capacity; suspend (p. 52) a weighed platinum crucible in the liquid, and precipitate the copper upon it. The total dilution, during the decomposition, should not exceed 150 c. c. As much as 5 per cent. of nitric acid can be present; the current should give 0.5 c. c. electrolytic gas per minute. When all the copper is precipitated, washed, dried and weighed (p. 51), make the residual liquid alkaline with sodium hydroxide, and add sufficient potassium cyanide to redissolve the precipitate. Electrolyse as directed (p. 55). Copper and cadmium can also be separated in solutions of their double alkaline cyanides (Jr. An. Ch., **3**, 385). Five to six grams of potassium cyanide should be added for every 0.2–0.4 gram of metal. Do not work with less than 200 c.c of liquid, and the current should not exceed 0.28 c. c. of electrolytic gas per minute. Under these conditions the cadmium is deposited, while the copper remains dissolved. Very recent experiments, made in this laboratory, show that also in the presence of an excess of free sulphuric acid the current will precipitate copper free from cadmium: *e.g.*, 0.1975 gram of metallic copper, and 0.1828 gram of cadmium, both as sulphates, were dissolved in 20 c.c. of water; to this were added 10 c.c. of sulphuric acid, of 1.09 sp. gr. and 100 c.c. of water. The current gave 0.30 c.c. electrolytic gas per minute. The precipitated copper weighed 0.1976 gram; it contained no cadmium.

It is not possible to separate these metals when present together in an oxalate solution.

The precipitation of copper in nitric acid solutions further enables us to separate it from iron, aluminium, chromium, cobalt, nickel, zinc, the alkaline earth and the alkaline metals, though it would perhaps be better to execute the separation from the first six in a solution containing free sulphuric acid. From mercury, silver and bismuth the copper cannot be separated in the presence of nitric or sulphuric acid. For the electrolytic separation of copper from mercury see p. 97. Its separation from bismuth has only recently been made possible by combining the behavior of copper in the presence of an excess of alkaline cyanide, and that of bismuth where it exists as a double citrate in an alkaline solution (p. 60). Add 3–4 grams of citric acid to the bismuth solution, so that upon the later addition of sodium hydroxide to alkaline reaction a precipitate is not produced. Into this liquid introduce the cyanide copper solution, and electrolyse with a current giving 0.15 c.c. electrolytic gas per minute.

In a solution of copper and lead, containing 5 per cent. of nitric acid, the former will be deposited completely at the cathode, while the latter is fully precipitated as dioxide at the anode (p. 62). This course is adopted when separating these metals in alloys or minerals (p. 63).

The separation of copper from manganese should be conducted in solutions containing a slight excess of sulphuric acid. While the copper is deposited as such upon the cathode, the manganese separates upon the anode as dioxide (p. 76). A platinum foil may be used as anode in this separation. Another method, applicable here, is based on the observation that manganese remains dissolved in the presence of phosphoric acid, while the copper is deposited in its usual form. For example, 0.1770 gram copper and 0.1500 gram manganese, both as sulphates, were treated with 30 c.c. of sodium phosphate, of sp. gr. 1.0388, and 10 c.c. phosphoric acid, of sp. gr. 1.347, then diluted to 150 c.c. with water and electrolysed with a current giving 1 c.c. of electrolytic gas per minute. The precipitated copper weighed 0.1765 gram. Manganese did not separate, even as dioxide. (See Am. Ch. Jr., **12**, 329.)

The deposition of copper in the presence of antimony is yet unsatisfactory. When the latter does not exceed ⅓ of the quantity of the first, no fault can be found with the separation (p. 39, and Wrightson, Z. f. a. Ch., **15**, 297).

As to the separation of copper from arsenic, Classen remarks (Ber., **15**, 297), that when the arsenic exceeds 0.20 per cent., the deposited copper is more or less dark in color, and the result will be high. Some chemists have advised that after the copper deposit has been dried, it should be heated to volatilize the arsenic; the residual cupric oxide is redissolved and its solution again electrolysed. This procedure will be satisfactory when arsenic is present in traces, otherwise it is worthless. The arsenic in copper ores can be entirely removed by evaporating their acid solution with bromine, when it will be expelled as bromide. The copper results are then satisfactory.

McCay (Chemiker Zeitung, **14**, 509) has observed that when the current from 4–6 Meidinger cells is conducted through a potassium arsenite solution, made distinctly alkaline with ammonium hydroxide, this salt sustains no change. With copper, under like conditions, the separation of the metal is quantitative. Upon this behavior he bases a very excellent separation of these two metals. The only care necessary is to see that not too much ammonia is employed. In this laboratory like results were obtained, but preference has since been given to the following course: Add the copper solution to that of the alkaline arsenite or arsenate, and follow it with a solution of potassium cyanide until the precipitate first produced is just dissolved; the liquid will then show a slight purple tint. A current of 0.25 c.c. electrolytic gas per minute, precipitates the copper quite rapidly under these conditions; the deposit will contain no arsenic (Am. Ch. Jr., **12**, 428).

When antimony, arsenic and tin are associated with copper, treat the sulphides with sodium sulphide. The resulting alkaline sulphide solution can then be employed for the separation of the first three (p. 102), while the insoluble copper sulphide may be dissolved and treated as described on page 54.

CADMIUM.

The methods already described under copper are sufficient for the separation of cadmium from this metal. A solution containing free nitric acid is used for the separation of cadmium from silver, mercury, lead and bismuth; the latter is also separated from it by using a solution in which there is a slight excess of sulphuric acid (p. 60). When these metals have been removed from their solution, neutralize the excess of acid with potassium hydroxide, add a slight excess of potassium cyanide and electrolyse the liquid for the estimation of the cadmium, as directed on page 55.

When there is an excess of but 2 c.c. of sulphuric acid, of sp. gr. 1.09, cadmium can be precipitated (p. 55), and thus separated from iron, aluminium, chromium, zinc, cobalt, nickel and manganese (the latter deposits at the same time as dioxide upon the anode, p. 76). Another method which serves for the separation of cadmium from either zinc or cobalt, consists in having these metals in solution in the form of double cyanides with the alkaline cyanides. The volume of the aqueous solution should be at least 200 c.c.; to this add 4½ grams of potassium cyanide, and electrolyse the liquid with a current giving 0.30 c.c. electrolytic gas per minute (Am. Ch. Jr., **11**, p. 352). Cadmium cannot be separated from nickel by this method.

Under the special methods given for the estimation of cadmium (p. 55) it was mentioned that it separates well from solutions of the acetate. Yver (B. s. Ch. Paris, **34**, 18) has employed this behavior to separate cadmium from zinc. The method is this: the metals are converted into acetates by the addition of 2–3 grams of sodium acetate to their solution, followed by several drops of free acetic acid. This liquid is then exposed to the current from two ordinary Daniell cells. Heat (70°) the solution during the decomposition. The precipitated cadmium contains no zinc. Three to four hours are necessary for the reduction of 0.18–0.210 gram of cadmium. Remove the zinc from the filtrate by the method of Richè (p. 71). Smith and Knerr (Am. Ch. Jr., **8**, 210) have tried this separation, and recommend that the current should not exceed 0.1–0.2 c.c. of electrolytic gas per minute. It is also essential that the liquid be held at a nearly uniform temperature (70°) during the reduction. The dilution of the liquid should not exceed 100 c.c.

The same chemists also (Am. Ch. Jr., **8**, 210) found that upon electrolysing a solution of these two metals, to which 3–4 grams of sodium tartrate and tartaric acid had been added, with a current of 3–4 c.c. electrolytic gas per minute, the cadmium was deposited completely from the warm solution, and contained no zinc.

Eliasberg (Z. f. a. Ch., **24**, 550) has also proposed a method for the separation of cadmium from zinc: Dissolve the metallic oxides in hydrochloric acid, evaporate their solution to dryness, add 8–10 grams of potassium oxalate, and 2–3 grams of ammonium oxalate, diluting finally to 100 c.c.; heat to boiling and electrolyse the warm (not boiling) liquid with a current equal to 0.15 c.c. electrolytic gas per minute. Cover the vessel in which the decomposition is made. Six to seven hours will be required for the complete deposition of 0.15 gram of metal (cadmium). The electrolytic separation of these two metals is also possible in a solution of their phosphates, dissolved in phosphoric acid (Am. Ch. Jr., **12**, 329).

To separate cadmium from antimony and tin it is necessary to have recourse to the usual method of analysis, the solubility of the sulphides of the first two in alkaline sulphides. A direct separation of cadmium from arsenic is possible, but that the cadmium may be precipitated absolutely free from arsenic, the latter must be present in the solution as an arsenate. Upon adding two grams of potassium cyanide to such a solution, and electrolysing the same with a current equal to 0.3 c.c. of electrolytic gas per minute, the cadmium will be completely precipitated in ten hours. The reduction is made in cold solutions (Am. Ch. Jr., **12**, p. 428).

MERCURY.

This metal is deposited quite rapidly from solutions containing free nitric acid (p. 57), hence under such conditions it may be separated from cadmium, iron, aluminium, chromium, zinc, nickel, cobalt, barium, strontium, calcium, magnesium and the alkalies. When lead and mercury are exposed, in a solution of nitric acid, to the action of the current, they are deposited simultaneously, the lead as dioxide at the anode (p. 62), and the mercury as metal upon the cathode. Manganese and mercury are separated to the best advantage in solutions containing free sulphuric acid (p. 76). Mercury cannot be separated in the electrolytic way from silver and bismuth. From copper, as long as the quantity of this metal does not exceed 20 per cent. of that of the mercury, the separation can be made in a cyanide solution (Jr. An. Ch., **3**, 254). As an example, it may be stated that 0.1833 gram mercury, as chloride, and 0.0259 gram copper, as sulphate, with 1.5 grams potassium cyanide, were diluted to 200 c.c. with water, and then electrolysed in the cold, with a current giving 0.32 c.c. of electrolytic gas per minute. At the end of sixteen hours 0.1833 gram mercury had separated.

More recent experiments, made in this laboratory, prove that mercury may be readily separated in the same way from zinc, nickel and cobalt. The quantity of alkaline cyanide to be used in these separations may vary from three to four grams, although when cobalt is to be separated from mercury good results will not be obtained if more than three grams of potassium cyanide are present for 0.3–0.4 gram of metal. The current should not exceed 0.8 c.c. of electrolytic gas per minute (Am. Ch. Jr., **12**, 104).

In separating mercury from tin and antimony, prepare their sulphides, and digest these with ammonium sulphide, dissolving out the first two. The residual mercury sulphide is then dissolved in aqua regia, and after neutralizing the excess of acid with an alkaline hydroxide, potassium cyanide is added in sufficient quantity to form the double cyanide, which is then electrolysed as described, p. 58. Mercury is separated from arsenic similarly to cadmium from this metal, although it is immaterial whether the arsenic exists in the solution as an arsenite or arsenate (p. 96).

BISMUTH.

At present there is no satisfactory electrolytic method known for the separation of this metal from mercury, silver and lead. Its separation from cadmium is effected in solutions containing free sulphuric acid (5–10 c.c. of sp. gr. 1.09), p. 60. This course will also serve to separate it from iron, manganese, zinc, nickel, cobalt, aluminium, chromium, uranium, magnesium and the alkaline metals (p. 60). The method of Eliasberg (p. 59) may also be used for the separation of bismuth from zinc, nickel, cobalt and uranium. In separating bismuth from those metals the sulphides of which are soluble in alkaline sulphides, it is necessary to have the usual gravimetric course precede the electrolytic reduction.

LEAD.

The deposition of lead as dioxide upon the anode (p. 62) in the presence of at least five per cent. of nitric acid affords a method for its separation from mercury, silver, copper, cadmium, iron, chromium, aluminium, zinc, nickel, cobalt, uranium, the metals of the alkaline earths and the alkaline metals. It will be remembered, of course, that some of these metals separate as such upon the cathode simultaneously with the lead upon the anode. Lead, in some respects, is much like manganese, from which it cannot be separated electrolytically. Its deposition requires no special description, as the conditions already described upon p. 63 are to be observed in the performance of the separations just indicated. Lead, tin, antimony and arsenic are separated as directed under the preceding heavy metals. Follow the ordinary gravimetric course.

Lead dioxide, like manganese dioxide (p. 76), is not separated from solutions containing an excess of an alkaline sulphocyanide, and, if already precipitated as dioxide, will redissolve upon the addition of the sulphocyanide.

SILVER.

To separate silver and copper electrolytically, mix equal quantities of the two metals, in the form of nitrates, with four and one-half grams of potassium cyanide, dilute to 200 c.c. with water, and electrolyse with a current, giving 0.15–0.80 c.c. electrolytic gas per minute (Am. Ch. Jr., **12**, 104). As much as 0.2 gram of silver will be deposited in 12–14 hours. If desirable, expose the filtrate containing the copper to the action of a stronger current (3 c.c. O-H gas per minute); as soon as the excess of alkaline cyanide is decomposed, the copper will be deposited in a dense and brilliant coating. Proceed as directed (p. 94) in separating silver from cadmium. There is no known electrolytic method for the separation of silver from mercury. It is true both can be precipitated from a nitric acid solution (pp. 57, 64), their joint weight determined, after which the mercury can be expelled by heat and the silver residue be re-weighed.

There is no electrolytic method known for the separation of silver from bismuth. The separation of silver from lead is made in a nitric acid solution (p. 64). A similar solution is used to separate it from the metals of other groups.

When antimony, tin and silver are present together, digest their sulphides with sodium sulphide, which will bring the antimony and tin into a proper condition to effect their separation electrolytically (p. 102). The insoluble silver sulphide is dissolved in nitric acid, and, after the excess of the latter is expelled, potassium cyanide is added in excess and the resulting liquid electrolysed in the cold, with a feeble current. The silver is deposited as a dense coating, and may be washed with hot water.

It is possible to separate silver from arsenic in the presence of three grams of potassium cyanide, providing the arsenic exists in the solution as an arsenate. A current, giving 0.30 c.c. electrolytic gas per minute, will be sufficient for the metallic reduction. Determine the arsenic in the residual liquid by the usual gravimetric method (Am. Ch. Jr., **12**, p. 428).

The course just described (above) for the separation of silver from copper will answer admirably for the same purpose with silver, zinc, nickel and cobalt. Not more than three grams of potassium cyanide are required for 0.2 gram of each metal. The total dilution should not be less than 200 c.c., and the current not stronger than 0.3 c.c. electrolytic gas per minute.

Much credit is due Classen and his co-laborers for valuable data upon the electrolytic separation of the following metals:—

ANTIMONY FROM TIN.

The sulphides (or residue from a solution of the metals) are placed in a weighed platinum dish, and covered with 60 c.c. of sodium monosulphide, to which is added one gram of sodium hydroxide. If immediate solution does not occur, apply heat, then *cool.* Conduct a current of 1.5–2.0 c.c. of electrolytic gas per minute through this mixture. When the reduction is finished, pour off the liquid into a second dish. Treat the antimony deposit as already directed (p. 87). To prepare the tin solution for electrolysis, proceed as described (p. 86) for the conversion of the sodium into ammonium sulphide (Ber., **17**, 2245; **18**, 1110).

ANTIMONY FROM ARSENIC.

These metals, or compounds of the same, are evaporated to dryness with aqua regia, the residue dissolved in 2–3 c.c. of water; concentrated sodium hydroxide is added so that there will be one gram of alkali present in the liquid, and finally add 60 c.c. of sodium monosulphide. Electrolyse as in the separation of antimony from tin (Ber., **19**, 323).

If antimony, arsenic and tin are present together, the arsenic is expelled from their solution by the Fischer-Hufschmidt method (Ber., **18**, 1110), and the separation of the tin and antimony made as already directed on the preceding page.

In general analysis phosphoric acid is frequently precipitated as tin phosphate. The latter, of course, contains oxide of tin. Dissolve the precipitate in ammonium sulphide. On electrolysing the solution the tin is precipitated, and the filtrate will contain all the phosphoric acid; this can be estimated in the usual way (Classen). By observing this suggestion the determination of the phosphoric acid in a separate portion of the material will not be required.

IRON, MANGANESE, ZINC, NICKEL, COBALT, ALUMINIUM, CHROMIUM AND PHOSPHORIC ACID.

Electrolytic methods for the separation of these metals are not either so numerous, nor so thoroughly worked out as with the metals already considered. Their separation from the heavy metals has been outlined under these, and it only remains to describe the courses which may be pursued with this group of metals when present together.

Concerning the separation of iron from manganese, it should be remembered that objections have been offered to the suggestion of Classen (Ber., **18**, 1787), hence to obtain results at all satisfactory it is advisable to carry out the separation *exactly* as given by this chemist: "If a solution of the double oxalates of iron and manganese is subjected to electrolysis, without the previous addition of a great excess of ammonium oxalate . . . . . : it is impossible to obtain a quantitative separation of the two metals, because the manganese dioxide carries down with it considerable quantities of ferric hydroxide. The complete separation of the metals is possible only when the separation of the dioxide is delayed till most of the iron is precipitated." The electrolysis in the *cold* is not favorable; the large amount of ammonium carbonate, or ammonia formed in the decomposition of the excessive ammonium oxalate dissolves the precipitated dioxide. "The rapid dissociation of ammonium oxalate when heated, however, gives a simple means of delaying, or entirely preventing, the formation of a manganese precipitate during the electrolysis." The solution containing the two metals is treated with 5–6 grams of ammonium oxalate, and while hot is acted upon with a current giving 15–20 c.c. of electrolytic gas per minute. Treat the iron deposit as directed on p. 78. Boil the liquid, poured off from the iron, with sodium hydroxide, to decompose the ammonium carbonate present, after which add sodium carbonate and a little sodium hypochlorite. The manganese is precipitated as dioxide, and finally weighed as the protosesquioxide. Nickel and manganese are separated from each other in a similar manner. Cobalt and zinc, when present with manganese, are separated from it by a current of 10 c.c. oxy-hydrogen gas per minute, acting in the cold. Oxalic acid is added toward the end of the reduction to redissolve any separated manganese dioxide.

To separate iron from zinc, add 1–3 c.c. of a solution of potassium oxalate (1 : 3) and 3–4 grams of ammonium oxalate to their solution, and electrolyse the liquid with a current liberating 10–12 c.c. electrolytic gas per minute. The zinc is deposited first, and no difficulty is experienced, providing its quantity is less than one-third that of the iron present. Classen provides for this condition by adding a weighed amount of pure ferrous ammonium sulphate in excess. The same chemist precipitates iron and cobalt simultaneously from their double oxalate solution (conditions as above), takes the combined weight of the metals, dissolves them in acid and determines the iron by titration; the cobalt is found by difference. Nickel and iron are also deposited together (same as cobalt and iron) as an alloy, which is weighed, then dissolved in concentrated hydrochloric acid, the iron oxidized, and the ferric solution titrated with a stannous chloride solution. It will be observed that an electrolytic separation of zinc from cobalt and nickel, and the latter from each other is wanting.

The writer would recommend the following course in separating the metals of this group: Separate the iron from the manganese, zinc, nickel and cobalt, by precipitation with barium carbonate. Dissolve the iron precipitate in citric acid, and electrolyse the solution according to the directions given upon page 79. The filtrate, containing the zinc, manganese, nickel and cobalt, together with a little barium salt, is carefully treated with just sufficient dilute sulphuric acid to remove the barium. After filtering, electrolyse the filtrate in a platinum dish, connected with the anode of a battery, yielding 3–5 c.c. of electrolytic gas per minute. A weighed piece of platinum foil will answer for the cathode. The manganese is deposited as dioxide (p. 76); the other metals remain dissolved and can only be separated by one of the usual gravimetric methods. This course proved quite satisfactory in the analysis of the mineral franklinite, where, after having obtained the iron and manganese as described, the zinc was also determined electrolytically in the liquid poured off from the manganese deposit. If the solution containing these two metals be very slightly acid with sulphuric acid, they can be precipitated simultaneously—the zinc at the cathode, and manganese dioxide at the anode.

Iron can be further separated, in citrate solution, from aluminium, chromium and titanium (p. 79). The deposition should occur in a *cold* solution, with a current, liberating 12 c.c. electrolytic gas per minute. This method will also serve to separate iron from chromium and phosphoric acid. Classen separates iron, cobalt, nickel and zinc from manganese, chromium and aluminium by electrolysing their hot oxalate solution in the presence of a large excess of ammonium oxalate. The first four are deposited as metals, while the manganese dioxide upon the anode has carried with it some chromium, and should be dissolved, and the manganese reprecipitated by sodium hydroxide and sodium hypochlorite (p. 104). The main solution from the metals is digested until the excess of ammonia is expelled, when the aluminium hydroxide is filtered off; the chromate solution, then reduced with hydrogen sulphide in the presence of an acid, is precipitated with ammonium hydroxide. In all cases where it is necessary to add oxalic acid to redissolve the aluminium hydroxide, or manganese dioxide, the acid should be introduced without the interruption of the current. When phosphoric acid is present with the iron and manganese it will be found in the liquid (oxalate) from which the metals have been previously precipitated, and may be removed as ammonium magnesium phosphate.

Little can be said relative to the separation of the rarer metals; further investigation is required in this direction.

Quite recent experiments, made in this laboratory, show that mercury and palladium can be separated if present together in a solution containing not less than 3 grams of potassium cyanide for 0.2–0.4 gram of the metals. The current necessary here may vary from

0.08 c.c.–0.22 c.c. electrolytic gas per minute. Notwithstanding that cadmium and silver are easily precipitated from their double cyanide solutions, it is impossible to separate them from palladium. In fact, they appear to hasten the deposition of the latter metal.

Mercury, silver and cadmium, furthermore, can be separated from solutions containing excess of alkaline cyanide together with tungstic and molybdic acids, without carrying down any of the latter. The conditions most favorable for these separations are perfectly similar to those just given above (pp. 96, 98, 101) for the separation of these metals from arsenic (Am. Ch. Jr., **12**, p. 428).

3. OXIDATIONS BY MEANS OF THE ELECTRIC CURRENT.

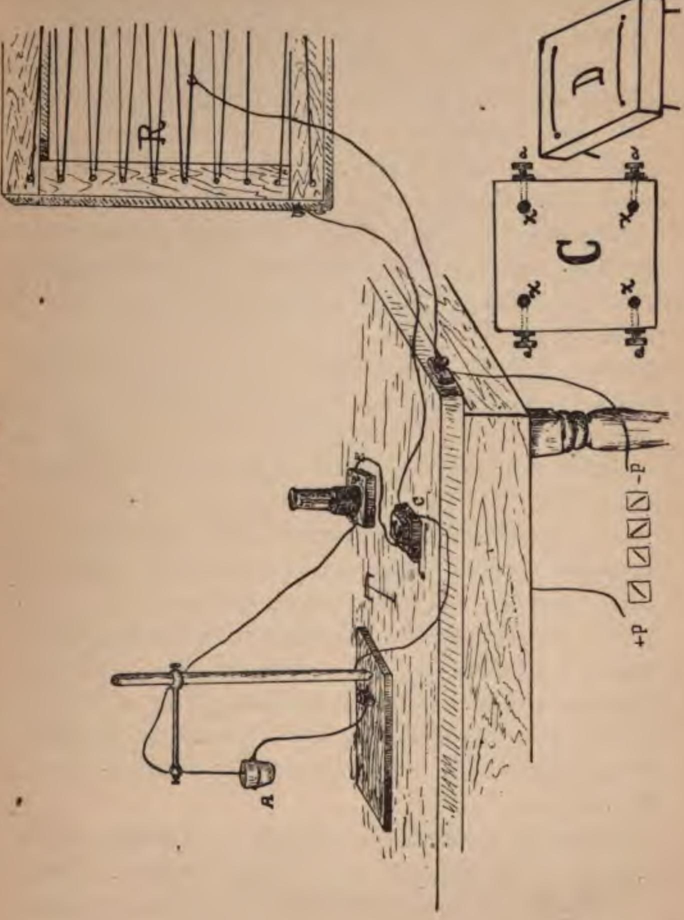
When natural sulphides, *e.g.*, chalcopyrite, marcasite, etc., are exposed to the action of a strong current in the presence of a sufficient quantity of potassium hydroxide their sulphur will be quickly and fully oxidized to sulphuric acid (Jr. Fr. Ins., April, 1889, Ber., **22**, 1019). The metals (iron, copper, etc.) originally present in the mineral separate as oxides and metal on dissolving the fused alkaline mass in water. This method of oxidation eliminates many other disagreeable features of the old methods. Its rapidity and accuracy entitle it to the following brief description:—

Place about 20 grams of caustic potash in a nickel crucible 1¼ inches high and 1⅜ inches wide. Apply heat from a Bunsen burner until the water has been almost entirely expelled, when the flame is lowered so that the temperature is just sufficient to retain the alkali in a liquid condition. The crucible is next connected with the negative pole of a battery, and the sulphide to be oxidized is placed upon the fused alkali. As some natural sulphides part with a portion of their sulphur at a comparatively low temperature, it is advisable to allow the alkali to cool so far that a scum forms over its surface, before adding the weighed mineral.

The heavy platinum wire, attached to the anode, extends a short distance below the surface of the fused mass. When the current passes a lively action ensues, accompanied with some spattering. To prevent loss from this source, always place a perforated watch-crystal over the crucible. After the current has acted for 10–20 minutes interrupt it. When the crucible and its contents are cold place them in about 200 c.c. of water, to dissolve out the excess of alkali and alkaline sulphate. Filter. Invariably examine the residue for sulphur, by dissolving it in nitric acid and then testing with barium chloride. The alkaline filtrate is carefully acidulated with hydrochloric acid, and after digesting for some time, is precipitated with a boiling solution of barium chloride. When the hydrochloric acid is first added, care should be taken to observe whether hydrogen sulphide or sulphur dioxide is liberated. If the oxidation is incomplete sulphur also makes its appearance as a white turbidity. The caustic potash employed in these oxidations should always be examined for sulphur and other impurities. As it is difficult to obtain alkali perfectly free from sulphur compounds, a weighed portion should be taken and its quantity of sulphur deducted from that actually found in the analysis.

The arrangement of apparatus employed in the oxidations just outlined is represented in Fig. 25. The crucible *A* is supported by a stout copper wire bent as indicated, and held in position by a binding screw attached to the base of a filter stand. The arm of the latter carries a second binding screw holding the platinum anode in position. While the platinum rod is generally the positive electrode, it is best to make it the negative pole for at least a part of the time during which the current acts. This is advisable because in many of the decompositions metals are precipitated upon the sides of the crucibles, and can readily enclose unattacked sulphide, so that by reversing the current (the poles) any precipitated metal will be detached, and the enclosed sulphide be again brought into the field of oxidation. Cinnabar is a sulphide which has a tendency to mass together, and it could only be decomposed and its sulphur thor-

FIG. 25.



oughly oxidized by reversing the current every few minutes. To reverse the current use the contrivance *C*; this is nothing more than a square block of wood fastened to the top of the table *T*, by a screw or nail. The four depressions (*x*) in it contain a few drops of mercury, into which the side binding screws (*a*) project. The mercury cups are made to communicate with each other by a cap of wood, *D*, carrying two metallic wires, which pass through it and project a slight distance on its lower side. By raising the cap and turning it so that the wires are vertical (↑) or horizontal (↣), the crucible or the platinum wire extending into the fused mass can be made the anode or cathode in a few seconds. *E* is a Kohlrausch amperemeter (Fig. 15), and *R* the resistance frame (Fig. 13).

Storage batteries furnish the most satisfactory current for work of this character. In the sketch the cells stand beneath the table; the wire from the anode passes through a hole in the table top, and is attached to one of the binding posts of the block *C*, while the positive wire is attached to a binding post at the end of the table top, and from here it passes to the resistance frame *R*, where it is fixed by an ordinary metallic clamp.

For most purposes the strength of current need not exceed 1–1.5 amperes per minute; however, it may be necessary occasionally to increase it to 4 amperes per minute. Pyrite, FeS_2, is even then not completely decomposed. This particular case requires the addition of a quantity of cupric oxide equal in weight to the pyrite, and a current of the strength last indicated before all of its sulphur is fully converted into sulphuric acid.

By increasing the number of crucibles it will be possible to conduct at least from four to six of these decompositions simultaneously, and by using a volumetric method for estimating the sulphuric acid, a sulphur determination can easily be executed in forty minutes.

Experience has demonstrated that 0.1–0.2 gram of material will require about 20–25 grams of caustic potash.

The arsenic in minerals is rapidly oxidized to arsenic acid by this method.

Chromite also seems to be rapidly decomposed when subjected to this treatment. Several quantitative experiments have been carried out, and the results obtained were very satisfactory.

INDEX.

AMPERE, 14
  Amperemeter, 31
Anions, 9
Anode, 9
Antimony, determination of, 87-89
  separation from arsenic, 102
    bismuth, 99
    copper, 92, 94
    lead, 99
    mercury, 98
    silver, 101
    tin, 102
Arsenic, determination of, 89
  separation from antimony, 102
    bismuth, 99
    cadmium, 96
    copper, 92
    lead, 99
    mercury, 98
    silver, 101
    tin, 103

BATTERY, Bunsen, 19
  Crowfoot, 17
  Daniell, 17
  Grenet, 14
  Grove, 19
  Leclanché 16
  Meidinger, 17
  storage, 24
Bismuth, determination of, 59-61
  separation from aluminium, antimony, arsenic, cadmium, chromium, cobalt, iron, manganese, nickel, tin, uranium, zinc, 98-99
  separation from copper, 91

CADMIUM, determination of, 54-57
  separation from aluminium, antimony, arsenic, bismuth, cobalt, iron, manganese, mercury, nickel, silver, tin, uranium, zinc, 94-97
  separation from copper, 90
    molybdenum and tungsten, 108
Cathions, 9
Cathode, 9
Cobalt, determination of, 72-75
  separation from bismuth, 99
    cadmium, 94, 95
    copper, 91
    iron, 105, 106
    manganese, 104
    mercury, 97, 98
    silver, 101
Copper, determination of, 47-54
  separation from aluminium, 90, 91
    antimony, 92, 94
    arsenic, 93
    bismuth, cobalt, iron lead, nickel, uranium, zinc, 91
    cadmium, 90
    manganese, 92
    mercury, 97
    silver, 100
    tin, 94
Current, action upon compounds, 10

ELECTROLYSIS, defined, 9

GOLD, determination of, 85

HISTORICAL account, 32-46

IRON, determination of, 78-80
  separation from aluminium, 106
    bismuth, 99
    cadmium, 94
    cobalt, 105
    copper, 91
    lead, 99
    manganese, 103
    mercury, 97
    nickel, 105, 106
    silver, 64
    zinc, 105

LEAD, determination of, 62–63
separation from aluminium, 99
antimony, 99
arsenic, 99
cadmium, 99
cobalt, 99
copper, 91, 99
iron, 99
mercury, 97, 99
nickel, 99
silver, 99, 100
uranium, 99
zinc, 99

MAGNETO-machines, 21

Manganese, determination of, 75–78
separation from aluminium, 105, 106
bismuth, 99
cadmium, 94
cobalt, 106
copper, 92
iron, 103, 105
mercury, 97
nickel, 106
zinc, 106
Mercury, determination of, 57–59
separation from aluminium, cadmium, copper, iron, lead, 97
antimony, arsenic, tin, 98
from cobalt, nickel, zinc, 97, 98
molybdenum, 108
palladium, 107
tungsten, 108
Molybdenum, determination of, 84
separation from cadmium, mercury and silver, 108

NICKEL, determination of, 72, 75
separation from aluminium, 106
bismuth, 99
cadmium, 94
cobalt, 94, 95
copper, 91
iron, 105, 106
lead, 99
manganese, 106
mercury, 97, 98
silver, 101

OHM, 13
Osmium, 37
Oxidations by means of the current, 108

PALLADIUM, determination of, 83
separation from mercury, 107
Platinum, determination of, 82, 83
Phosphoric acid, separation, etc., 103, 107

RESISTANCE coils and frames, 26, 27, 28

SILVER, determination of, 63–67
separation from aluminium, copper, iron, lead, manganese, uranium, 100
antimony, arsenic, cobalt, nickel, tin, zinc, 101
cadmium, 94
molybdenum and tungsten, 108
Sulphur, oxidation of, 108, 109

TANGENT galvanometer, 30
Thallium, determination of, 81
Thermo-electric pile, 21
Tin, determination of, 85, 86
separation from antimony, 102
arsenic, 103
bismuth, 99
cadmium, 96
copper, 94
lead, 99
mercury, 98

URANIUM, determination of, 80

VOLT, 14
Voltameter, 29

ZINC, determination of, 67–72
separation from aluminium, 106
bismuth, 99
cadmium, 94, 95, 96
copper, 91
iron, 105
lead, 99
manganese, 106
mercury, 97, 98
silver, 101

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